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1998

THE PRINCIPLES OF MATHEMATICAL CHEMISTRY.

THE ENERGETICS OF CHEMICAL PHENOMENA

BY

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AUTHORIZED TRANSLATION FROM THE GERMAN

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TRANSLATOR'S PREFACE.

In presenting this work to the English-speaking public, the translator is actuated by the desire to spread the knowledge of Physical Chemistry more widely among students and chemists. The knowledge gained by it is of undoubted value, in all parts of chemical science, and is gaining in importance daily; and the time is coming when no chemist, whatever his branch, will be considered completely equipped without it. In translating, the text has been followed as closely as possible, and clearness rather than literary style has been the aim. Dr. Helm has been so good as to read the work, and the thanks of the translator can best be expressed to him in this place.

PREFACE TO THE GERMAN EDITION.

THE title "Mathematical Chemistry" means that the purpose of this little book is to collect the results, according to the deductive method, of the investigations in the realm of general chemistry.

The subject of the mathematical consideration of nature, which in its earlier development was known as Physical Chemistry, can now, in its present state, be viewed from a general theoretical standpoint as a whole; and in this state it appears as one of the clearest and most complete proofs of the principle of the conservation of energy. The fact that single parts of mathematical chemistry are derived from other reasoning, without regard to, or with mere passing consideration of, this general principle—as, e.g., the conception of the Osmotic Pressure from the analogy to gases, or from hypothetical molecular theories—can be attributed to the difference in the points of departure of these investigations, and also to the earlier lack of recognition of the Theory of Gibbs.

The return to Willard Gibbs and—as far as concerns thermodynamics proper—to Horstmann appears to me to be a purification of the scientific structure

from conceptions which have become unnecessary to it. In the light of fewer conceptions—held together by the principle of energy—we have a complete view of the whole, which is particularly desirable in a first introduction to the subject.

The presence of experiments in this book could hardly be allowed ; for they do not here, as in the case of the inductive presentation, lead to the formation of the ideas, but only serve to elucidate them and to make the reader familiar with their application. On the other hand, Ostwald's very complete book relieves the author from dwelling upon the details of the single investigations. If I, according perhaps to the taste of some of my readers, have restricted myself too much in this respect, it is with the hope that, by it the leading conception, in each case, may be the more prominent, and impress itself upon the student by the simplicity of its application.

GEORG HELM.

DRESDEN, *Aug.* 1894.

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THE PRINCIPLES OF MATHEMATICAL CHEMISTRY.

PART I.

ENERGY.

CHAPTER I.

THE APPLICATION OF THE PRINCIPLE OF THE CONSERVATION OF ENERGY TO CHEMICAL REACTIONS.

THE basis of the mathematical treatment of chemical phenomena is the principle of the conservation of energy,—which has shown itself in no branch of the mathematical knowledge of nature so valuable or sufficient as in those two nearly related processes, viz., thermal and chemical reactions.

The principle of the conservation of energy is best used for the study of chemical phenomena in the following form :*

The momentary state of a body or part of a body is determined by certain varying quantities, as co-

* For the gradual development of this treatment of natural phenomena see the author's Lehre von der Energie (Leipzig, 1887).

ordinates in space, velocity, temperature, electrical charge, etc., which are called *parameters* of that body. Then for each of the smallest particles of the body, in each instant, we have a certain varying quantity, its *intrinsic energy*,* which depends only upon the momentary state of the body, and which is therefore a function of a parameter. This function has the property by which every *possible* change in Nature can be considered as an increase of the intrinsic energy of some bodies and a decrease of the same in others, and by which the *total amount* of all intrinsic energies, by all changes in Nature, must remain *unchanged.*

The principle of the conservation of energy so expressed is not to be easily proven, but it presents to us a way of considering natural phenomena, the correctness of which can only be established by the results. Thus far, in very many cases, it has been possible to define the intrinsic energy of a body undergoing change in such a manner that this method has been shown to be possible, and indeed to be preferred; and experiments have always shown that the difference between two intrinsic energies, so defined, is independent of the means by which the one is transformed into the other.

As far as concerns chemical changes, Lavoisier and

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* The intrinsic energy of a body in a given state represents the mechanical value of all actions which the body would exert by transformation from a given state into the standard state, or the mechanical value of all efforts which are necessary to take the body from the standard state into the given state. (Wm. Thomson, Math. Phys. Papers, I, 292.)—TRANS.

Laplace, in 1780, considered it self-evident that all increase and decrease of heat which is shown by a change of state in a system of bodies is also shown in the reverse order when the system returns to its initial state. To be sure, this view was adopted from the experience of such reversible changes as solution and changes in the state of aggregation, by the reversal of which all the intermediate states follow in the reverse order. But it is just in the case of pure chemical reactions that this reversibility rarely occurs. Hess,* however, in 1840, proved that, in general, two chemical reactions that transform the state *A* into the state *B* develop the same amount of energy; i.e., the difference in energy between the states *A* and *B* depends only on these states, and not upon the nature of the transformation. He transformed H_2SO_4 by addition of water into a certain hydrate of sulphuric acid, and this by addition of ammonia into a water solution of ammonium sulphate. He found by this that when the reaction took place in a calorimeter the same amount of heat was developed, within the limits of experimental error, independent of which hydrate had been formed first; and this amount was the same as that developed by the immediate formation of $(NH_4)_2SO_4 + Aq$ by the action of ammonia and pure sulphuric acid. These experiments have since, by more accurate methods of observation, been confirmed.

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* Pogg. Ann. 50. Ostwald's Klassiker d. exakt. Wiss., vol. IX.

CHAPTER II.

THE MEASUREMENT OF CHEMICAL ENERGY.

SINCE in all natural phenomena the intrinsic energies are only noticeable by their changes, the only possible way we have of measuring them is by their differences. As we cannot deprive a body of all its energy, it is impossible to measure all that is in it, and consequently we must be satisfied with the knowledge of how much it exceeds or falls short of the energy of that body in a certain definite state which we call the *standard state* (Normalzustand).

The simplest way of measuring the difference between the intrinsic energy of a body in the state A, e.g., the standard state, and another state, B, is to transform the one into the other in such a manner that the difference of energy appears in *one* form,—as heat, in a calorimeter. In this way, in many cases, we can measure directly the difference of energy in the chemical reaction by the heat generated.

As unit of heat or calorie (cal.), it is best to choose, in accord with the other units employed, the heat energy which is necessary to warm the mass of one gram of water 1° Celsius (air-thermometer).

Since the specific heat of water is a function of the temperature, it is necessary, further, for an exact defi-

nition, to settle on some one temperature from which the heating of the water 1° Cel. shall follow. For this purpose we can choose either 0° Cel. as the initial temperature, in which case the unit of heat is known as the *zero calorie* (Nullkalorie); or we can choose the one-hundredth part of the amount of heat necessary for the heating from 0° to 100° Cel., which unit is called the *mean calorie* (mittlere Kalorie); or, finally, we can choose the most convenient temperature for observation, that between 15° and 20° Cel., as the initial temperature (Gebrauchskalorie). For the definition of a practical unit, the one proposed by Dieterici * for a mean calorie, as determined with an ice-calorimeter, is to be recommended: it is the heat necessary to melt such an amount of ice at 0° Cel. as to cause a decrease of volume equal to that of 15.44 mg. of mercury. The small differences which occur in the sizes of the different calories are, in the present state of thermochemical measurements, of little importance; but for the calculation of the constants they must be considered. 1 mean calorie = 1.0045 zero-calories.

Since the differences of energy in thermochemistry, when measured in any of the above-defined units, are very large, and are not exact to more than three or four hundred units, larger ones have been proposed. These are the *Ostwald calorie*, K,† and the *large calorie*,

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* Wied. Ann. 33, 1888.

† Wied. Ann. 33, 1888. The Ostwald calorie, K, is equal to 100 mean calories at 18° Cel.; it is equal to, at Baltimore, 4183 megergs. See Ostwald, Lehrbuch d. Allgemeinen Chemie, vol. II, i, p. 74 (Leipzig, 1893).—THE TRANSLATOR.

Cal., which are, respectively, one hundred and one thousand times as great as the above-defined *small calorie*, cal. Between these units we then have the following relations :

$$1 \text{ cal.} = 1 \text{ g.}^\circ \text{ Cel.}$$
$$1 \text{ K.} = 100 \text{ g.}^\circ \text{ Cel.}$$
$$1 \text{ Cal.} = 1000 \text{ g.}^\circ \text{ Cel.}$$

For the clear and complete expression of the results of observations on chemical energies we must still find proper units for the amounts of matter in which these energies are stored. Stoichiometry has led—in addition to the knowledge that these amounts are proportional to the masses or weights*—to proportional numbers, the molecular weights, which are specific properties of the single chemical elements, and are expressed by the chemical formulæ. Chemical energetics uses the same symbols. The chemical symbols of substances must in this case represent as many *grams* as are expressed by the molecular weight; in other words, the so-called gram-molecule or mol (Ostwald). It is easier for chemical purposes to measure an amount of water in this way than in grams; the specific constant or mol being here 18 grams, so that $n H_2O$ is equal to $18n$ grams. The consequence of this is, that the symbols of the atoms also represent

* Weight is here used in the same sense as mass, therefore different from gravity. The original conception of mass established its relation to kinetic energy, as Ostwald has already observed ; that is, stands also in relation to potential and to chemical energy as the result of experience.

certain masses: H means 1 gram of hydrogen; O, 16 grams of oxygen; and O_2, 32 grams, etc.

The chemical symbols in energetics represent, in addition to the specific units of mass, also the *intrinsic energies* that these units of mass contain. That 18 grams of fluid water contain, at the same temperature, less energy than 2 grams of hydrogen plus 16 grams of oxygen, from which it is formed, and so much less as is represented by 68000 cals., can now be shown by the formula

$$\underbrace{2H + O}_{\text{gaseous}} = \underset{\text{liquid}}{H_2O} + 68000 \text{ cals.}$$

or

$$2H + O - H_2O = 68000 \text{ cals.}$$

The appearance of an amount of energy in the formula shows us that here the chemical symbols are used in the second meaning also, and not only as a number of units of mass.

If by the combustion of hydrogen (in a calorimetrical bomb) only heat is developed, and this heat is not used up in altering the temperature of the products of the reaction, then by the formation of every 18 grams of water 68 cals. of heat will be liberated. If, on the other hand, some of the energy is developed in another form, then the amount of heat is the same as it was before, *less* the amount of heat which the other form of energy corresponds to. The formula as given means only that the *difference* of energy between the states

$2H + O$ and H_2O is; for every 18 grams of the latter formed, 680 K.

The explanation of all the conditions to be observed in the formation and use of equations of chemical energy is the object of the next chapter, and of some of those following.

It will be well, however, to state here the effect which the differences in the atomic weights have upon the values of the differences of energy. If we assume $O = 16$, then the most probable value for H will be 1.0032; by a small calculation we find that the difference in energy between water and its components, by these values, is 24 cals. larger; and if we choose $H = 1$, $O = 15.95$, then the difference will be 189 cals. smaller; than that value given in the equation.

It may be well to remark here that the amount of heat which expresses the difference of energy for a gram-molecule or mol. is called the *heat of reaction by constant volume.** It is reckoned positive when the intrinsic energy of the reaction decreases, and is called, according to the chemical or physical nature of the reaction, the heat of aggregation, solution, modification, dilution, or combustion. The study of the determination of these differences of chemical energy is known as *Thermochemistry.*

It will be well, perhaps, to append here a few calculations, which are possible from the few principles of

* Here in the calorimetrical bomb the volume is constant, and hence the above designation. In case of H burning in open air, under atmospheric pressure, the amount of energy would be different from this, as will be explained later.—TRANS.

thermochemistry that have already been explained, and thus to make the student familiar with their application.

If H_2SO_4 unites with nH_2O, we have, according to J. Thomsen, an amount of heat equal to:

$$\left\{ \frac{n}{n + 1.798} \right\} 17860 \text{ cals.}$$

This formula, from experiment, shows small variation, except for medium concentrations, between, for example, $n = 50$ and $n = 1000$. How much heat, R, will be developed, according to this, by the admixture of xH_2SO_4 with mH_2O, providing that the change of volume, by the mixing, brings with it no noticeable change in the difference of energy?

R is plainly x times as great an amount of heat as $1H_2SO_4$ with $\frac{m}{x}$ H_2O would liberate; therefore, since $\frac{m}{x} = n$,

$$R = x \frac{\frac{m}{x}}{\frac{m}{x} + 1.798} . 17860 = \frac{mx}{m + 1.798x} . 17860 \text{ cals.}$$

What amount of heat will be produced by the addition of the very small quantity dx of the acid to the mixture of $x . H_2SO_4$ and $m . H_2O$; and, on the other hand, what amount by the addition of the very small quantity, dm, of water?

By differentiating,* we find

$$\frac{\partial R}{\partial x}dx = \frac{m^2}{(m+1.789x)^2} \cdot 17860 \cdot dx$$

$$= \frac{n^2}{(n+1.798)^2} \cdot 17860 \cdot dx.$$

$$\frac{\partial R}{\partial m}dm = \frac{1.798x^2}{(m+1.798x)^2} \cdot 17860 \cdot dm$$

$$= \frac{1.798}{(n+1.798)^2} \cdot 17860 \cdot dm.$$

Up to what dilution does a drop of H_2SO_4 bring a greater amount of heat than a drop of H_2O of the same weight?

If both drops weigh the same, let us say dM grams, then the drop of H_2SO_4 contains

$$dx = \frac{dM}{98}$$

gram-molecules· the drop of water, however, contains

$$dm = \frac{dM}{18}$$

gram molecules. Now $\frac{\partial R}{\partial x}dx \gtrless \frac{\partial R}{\partial m}dm$, according as $n^2 \gtrless 1.798\,dm$, or

$$n^2 \gtrless \frac{1.798 \times 98}{18}, \quad n \gtrless 3.1$$

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* Horstmann, Theor. Chemie in Graham-Otto's Lehrbuch, II, 1885.

If one adds to a mixture of x. H_2SO_4 and m. H_2O, dx. H_2SO_4 and dm. H_2O at the same time, then

$$dm : dx = m : x = n,$$

or no other development of heat than that caused by the mixing of the small portions dm and dx.

How much heat, Q, is formed when the dilute acid $HCl.nH_2O$ is added to an unlimited amount of water? From J. Thomsen we have

$$HClH_2O + (n-1)H_2O = HCl.H_2O,(n-1)H_2O + \frac{n-1}{n}119.8\,K;$$

and it follows, when we substitute for n its value ∞, that

$$HCl.H_2O + Aq = HCl.H_2O, Aq + 119.8\,K.$$

On the other hand, the amount of heat, Q, must satisfy the equation

$$HCl.H_2O + (n-1)H_2O = HCl.H_2O,Aq + \frac{n-1}{n}119.8 + Q,$$

where we can calculate $(n-1)H_2O$ as Aq.

By subtracting the one from the other we find

$$Q = \frac{119.8}{n}\,K;$$

while Berthelot* found by experiment

$$Q = \frac{116.2}{n}\,K.$$

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* See Planck, Grundriss der allg. Thermo-chemie in Ladenburg's Hand-wörterbuch der Chemie, 1893. Also published separately as a small book.—TRANS.

The foregoing examples show, by their application of the principle of the conservation of energy, without further aids, that all reactions or series of reactions that transform one substance into another must liberate the same amount of energy, which is the difference of the intrinsic energies of these substances. If they lead, on the one hand, to the confirmation of the principle of the conservation of energy, they lead also, on the other, to the determination of the energy differences of reactions which are not directly accessible to observation; especially, in many cases, to the difference of energy between a substance and its elementary constituents, the so-called *heat of formation* (Bildungswärme). Since from the difference of energy between a compound and its elements we can find, by subtraction, the energy of the compound (i.e., the difference between its state and the standard state), thermochemistry reaches its greatest value, as far as concerns chemical equations proper, by the determination of the heats of formation.

Thus, for example, from the heats of formation and of solution of magnesium chloride and of sodium chloride,

$$Mg + Cl_2 = MgCl_2 + 151 \text{ Cal.},$$

$$Mg + Cl_2 + Aq = MgCl_2Aq + 187 \text{ Cal.},$$

$$Na + Cl = NaCl + 98 \text{ Cal.},$$

$$Na + Cl + Aq = NaClAq + 97 \text{ Cal.},$$

we can find the heats of reaction, Q and Q', of the chemical process between $MgCl_2$ and Na.

If we substitute in the equation

$$MgCl_2 + 2Na = 2NaCl + Mg + Q,$$

the values for $MgCl_2$ and NaCl, as found in the first and third equations, we obtain

$$Mg + Cl_2 - 151 + 2Na = 2Na + 2Cl - 2\times 98 + Mg + Q,$$

$$\text{or} \qquad Q = 45 \text{ Cal.}$$

In the same way we find, for the case that the reaction takes place in a water solution,

$$Q' = 7 \text{ Cal.}$$

From thermochemical data,

$$C + 2O = CO_2 + 97 \text{ Cal.};$$
$$CO + O = CO_2 + 68 \text{ Cal.};$$

therefore, by subtraction, we find the heat of formation of carbon monoxide,

$$C + O = CO + 29 \text{ Cal.}$$

In this case amorphous carbon is to be understood by C. If one wished to find an equation for one of the other modifications of carbon, the amount of energy would have to be changed, for the intrinsic energies of the elementary elements would change. One mol of amorphous carbon, of graphite, and of diamond give, respectively, by combustion,

97650, 94810, 94310 cals.,

which shows a difference of intrinsic energy of more than 3000 cal. for amorphous carbon and diamond.

J. Thomsen designates the heat of formation by a

symbol, so that, for example, the contents of the above equation for $MgCl_2$ would take the form

$$(Mg,Cl_2) = 151 \text{ Cal.},$$

where the parenthesis means that the chemical elements which are separated by the comma unite to form a compound. The symbol of Thomsen's also means, when used for constant volume, the excess of energy of the elements over the compound.

CHAPTER III.

CHANGES IN TEMPERATURE AND IN THE STATE OF AGGREGATION.

THE energy of a substance changes by each change of a chemical or physical nature which takes place in it. Therefore thermochemical equations, strictly considered, should be given not only in a special chemical state, but also in a special physical one, under which each of the reactions of the elementary substances takes place. We must know the pressure, temperature, aggregation, and allotropic state of each of the bodies which come under our consideration. As self-evident, when not otherwise expressly stated, it is to be understood in all thermochemical equations that the substances are in the standard state (Normalzustand), i.e., at 0° Cels. temperature and under the pressure of 1 atmosphere, and with no differences of intensity (e.g., electrical) existing.

The state of aggregation of a body is best distinguished by certain signs, as by different letters (Ostwald) or by brackets and parentheses, so that H_2O means steam, (H_2O) liquid water, and $[H_2O]$ ice. The specific heats necessary for providing for changes of temperature are, as are also the latent heats and heats

of aggregation, based generally in physics on the unit of mass, the gram; but in thermochemistry they must be recalculated and based upon the atomic and molecular weights. For instance, if c is the specific heat of a substance and m its molecular weight, then mc is the molecular heat, and ac the atomic heat if a is the atomic weight.

These general rules will be illustrated sufficiently by the following examples:

From Julius Thomsen's observations for $H = 1$ and $O = 16$, or $H_2O = 18$, we have the equation

$$2H + O = (H_2O) + 67484 \text{ cals.}; \quad 18° \text{ Cels., 1 atmosphere pressure.}$$

What would the equation be, if, instead of the temperature of observation, 18° Cels., we had any other, $\vartheta°$, still retaining the volume as it was at 18°?

The specific heats* of hydrogen, oxygen, and liquid water are expressed, for constant volume, by the equations

$$\underset{\vartheta°}{H_2} = \underset{18°}{H_2} + 4.82(\vartheta - 18);$$

$$\underset{\vartheta°}{O} = \underset{18°}{O} + 2.48(\vartheta - 18);$$

$$\underset{\vartheta_0}{(H_2O)} = \underset{18°}{(H_2O)} + 18(\vartheta - 18).$$

---

* These and the following corresponding data are taken from Regnault's observations, as collected by Zeuner in his Technischer Thermodynamik.

From these we obtain

$$\underbrace{H_2 + O - (H_2O)}_{\vartheta^\circ} = \underbrace{H_2 + O - (H_2O)}_{18^\circ} - 10.7(\vartheta - 18)$$
$$= 67484 - 10.7(\vartheta - 18)$$
$$= 67677 - 10.7\vartheta,$$

or

$$H_2 + O = (H_2O) + 67677 - 10.7\vartheta \left\{ \begin{array}{l} \text{Temp.} = \vartheta^\circ. \text{ Vol.} \\ \text{same as for } 18^\circ \\ \text{Cels.} \end{array} \right.$$

How great is the difference of energy between dry steam at ϑ° and its component gases H_2 and O at 0°?

We start from the specific heats at constant volume, and the energy differences, as given by *Zeuner*, between fluid water at ϑ° and steam at the same temperature. We have

$$\underset{0^\circ}{H_2} = \underset{18^\circ}{H_2} - 4.82 \times 18;$$
$$\underset{0^\circ}{O} = \underset{18^\circ}{O} - 2.48 \times 18;$$
$$\underset{\vartheta^\circ}{(H_2O)} = \underset{18^\circ}{(H_2O)} + 18(\vartheta - 18);$$
$$\underset{\vartheta^\circ}{H_2O} = \underset{\vartheta^\circ}{(H_2O)} + 18(575.40 - 0.791\vartheta).$$

By subtracting the last two equations from the sum of the first two, after eliminating the energy (H_2O), we find

$$\underbrace{H_2 + O}_{0^\circ} - \underset{\vartheta^\circ}{H_2O} = \underbrace{H_2 + O - H_2O}_{18^\circ} - 18(564.7 + 0.209\vartheta)$$
$$= 67484 - 18 \times 564.7 - 18 \times 0.209\vartheta$$

or
$$\underbrace{H_2 + O}_{0^\circ} = \underset{\vartheta^\circ}{H_2O} + 57319 - 3.76\vartheta.$$

By this equation the question is answered, but only so when the specific heats are considered as independent of the temperature.

It is possible to prove that in general the heat of formation is a function of the temperature of the same. (Kirchhoff.) If the intrinsic energies of the unit of mass of two substances at the temperature $\vartheta_0°$ are E_1 and E_2, and these substances unite in the amounts M_1 and M_2 at the temperature $\vartheta°$, at the same time setting free the amount of heat Q; and if after the reaction, when the temperature is again $\vartheta_0°$, the intrinsic energy for the unit of mass is E,—then by the principle of the conservation of energy we have

$$(M_1 + M_2)E =$$

$$M_1E_1 + M_2E_2 - Q + \int_{\vartheta_0°}^{\vartheta°}(M_1c_1 + M_2c_2)d\vartheta$$

$$+ \int_{\vartheta°}^{\vartheta_0°}(M_1 + M_2)cd\vartheta,$$

where c_1, c_2, and c are the specific heats, for constant volume, of the substances and the product respectively. If we allow the temperature $\vartheta°$ to vary, then

$$\frac{\partial Q}{\partial \vartheta} = M_1c_1 + M_2c_2 - (M_1 + M_2)c$$

which is in general not equal to zero, i.e., Q will in general vary also. For the combustion of H, when Q refers to one mol, we have, as already given above,

$$\frac{\partial Q}{\partial \vartheta} = -\ 10.7.$$

CHAPTER IV.

MECHANICAL ENERGY.

ALTHOUGH heat is the form of energy which is produced in the greatest amount by the chemical energy differences, still it is impossible, even in the most important cases, to shut out entirely the other forms. It is necessary first for us to study the changes of volume in chemical processes to find what amounts of energy they represent, and to do this we must consider all the phenomena of motion.

As far as concerns the motion of solid bodies, we must consider two forms. The *kinetic energy*, or the energy of motion of a body whose mass is mg and whose velocity is $c\frac{\text{cm.}}{\text{sec.}}$, is

$$\frac{1}{2}mc^2\,\frac{\text{g.cm.}^2}{\text{sec.}^2}.$$

Its unit is 1 g.cm.^{2}sec.$^{-2}$, and is called the Erg. If the body is located in a system of co-ordinates, and they change in the time dt by dx, dy, and dz, we can express the kinetic energy by the following equation:

$$\frac{1}{2}m\left[\left(\frac{dx}{dt}\right)^2+\left(\frac{dy}{dt}\right)^2+\left(\frac{dz}{dt}\right)^2\right].$$

Each change in the kinetic energy of a body is called work; for example, the mechanical work along the x co-ordinate in the time dt is

$$m\frac{dx}{dt}\frac{d^2x}{dt^2}dt = m\frac{d^2x}{dt^2}dx.$$

According to the principle of the conservation of energy, each change of this sort is an exchange of energy; and this has led to the conception of another form of energy, which acts as a source and an outlet to the kinetic energy. This form is called the *potential* energy.

The characteristic property of each potential energy is this, that its amount depends only upon the position of the movable body. On this account potential energy has been well called the energy of position. If the position of a body is changed, with respect to its co-ordinates, by the amount dx, dy, and dz, then the total change of its kinetic energy is given by the three parts Xdx, Ydy, and Zdz, and the factors, X, Y, and Z are the components of a vector which is the force which acts upon the mass. The unit of force is the Dyne, or 1 g.cm.sec.$^{-2}$

The comparison of the expressions of mechanical work show that

$$X = m\frac{d^2x}{dt^2}, \quad Y = m\frac{d^2y}{dt^2}, \quad Z = m\frac{d^2z}{dt^2},$$

or $$\text{Force} = \text{Mass} \times \text{Acceleration}.$$

Of the two factors which are necessary for the measurement of kinetic and potential energy, or for

the measurement of kinetic energy and its changes, besides those of space and time, the one is determinable from the other when the acceleration is known. It is especially easy from the above to find the amount of a force when we know the mass and the acceleration. In the same way we could determine the mass if we chose a unit of force to start with. In technology this latter method is preferred. Here neither the mass nor, what is practically the same, the weight of 1 cubic centimeter of water is chosen as the unit of force, but the acceleration of this body, due to gravitation, as is shown in some certain place on the earth, the *standard place.* The units derived from gravitation are distinguished by stars, *, from the units of mass. Thus we have

$$\text{Unit of force} = \text{Unit of mass} \times \left\{ \begin{array}{c} \text{Acceleration of} \\ \text{gravitation in the} \\ \text{standard place} \end{array} \right\},$$

or $\text{Grams} \times \text{Gravitation} = \text{Grams} \times \text{Mass} \times 981 \frac{\text{cm.}}{\text{sec.}^2}$.

$$g^* = 981 \text{ g.cm.sec.}^{-2}$$
$$= 981 \text{ dynes.}$$

The corresponding amount of energy is

$$\text{Grams} \times \text{Gravitation} \times \text{cm.} = \text{g.*cm.} = 981 \text{ ergs,}$$

and is the 100000th part of the kilogrammeter (properly kilogram × gravitation × meter) Kg^*m, which represents the energy that must be expended to raise 1 kilogram 1 meter in the air.

The energies of position which occur in Nature are divided (Ostwald) into distance, surface, and volume

energy. In the first case the changes of energy are proportional to the changes of distance between a pair of bodies, and they exert either an attracting or a repelling force. Gravitation and several kinds of electric and magnetic energies belong to this group. The second group, as was the first, is also of little importance in our present work, for surface energy is proportional to the surface, which is in a state of tension.

On the other hand, the volume energy is of extreme importance in thermochemistry, because it can be transformed directly into kinetic energy, and also into heat. Liquid and gaseous bodies, which, on account of their simplicity, only will be treated here, show the property that when an increase of volume, and no other change, takes place the intrinsic energy decreases. The proportion of this decrease of energy $-dE_v$ to the increase of volume, dV, is placed equal to the pressure p, so that

$$-\frac{dE_v}{dV} = p, \quad dE_v = -pdV,$$

and therefore

$$\text{Unit of pressure} = \frac{\text{Unit of energy}}{\text{Unit of volume}} = \frac{g}{\text{cm.sec.}^2}, \text{ or } \frac{g^*}{\text{cm.}^2}.$$

The pressure, so defined, can also be considered—and this is the usual way—as a force which does work against resistance. We imagine the surface of the liquid or gaseous body under consideration as immovable except in the small area of the size q sq. cm. A small increase of volume is then only possible by a movement outward of this area in the direction of its

normal, let us say of the amount dn (Fig. 1), so measured that $dV = q \,.\, dn$. If there is a force, P, directed downward in the direction of the normal of the surface which works against this outward pressure, then during the expansion dV the mechanical work done will be Pdn. From the principle of the conservation of energy

FIG. 1.

$$dE_v = -pdV = -Pdn\,;\dagger$$

but $dV = -qdn$, and therefore

$$p = \frac{P}{q};$$

i.e., the pressure can be considered as the force necessary to stop entirely the increase of volume.

It is now only necessary to give the relation between the calorie, as described in a previous chapter, and the erg or the technical kilogrammeter. From Joule's very careful experiments,

1 Cal. = 423.55 tech. kilogrammeters;

1 cal. $= 42355 \times 981$ ergs $= 415.5 \times 10^6$ ergs.

The latest experiments by Dieterici, by which the mechanical equivalent of heat was determined from the heat developed by the electrical current, give the value of the practical mean calorie for mean latitudes as

1 cal. $= 424.36 \times 10^6$ ergs,

1 Cal. = 432.5 tech. kilogrammeters,

† Counted negative because done by the fluid, and consequently lost by it; if from the outside, thus compressing the fluid, it would be positive, for then it would be added to that of the fluid.—TRANS.

with a probable error of 0.17 for the number 424.36. The exact recalculation of the earlier results of Joule, by help of the data of Dieterici, is difficult, for the reason that the conception of 1° Cels. is uncertain; that is, the reduction of the readings on the mercury-thermometer to the air-thermometer.

CHAPTER V.

THE VOLUME ENERGY OF GASES.

FOR use in thermochemistry, we need the mechanical considerations treated of in the last chapter only so far as to be able to bring into calculation the volume energy of gases which are present in chemical reactions.

As long as a body remains solid or liquid it undergoes such a small change of volume that the changes of energy can be neglected when, as usual, the reaction takes place under ordinary pressures. Even in the case of gases, where these changes of volume are so large, the corrections are so unimportant, in the present state of thermochemical methods, as to affect only the last certain figure of the results.

Gaseous bodies, when brought sufficiently high above their critical states, follow the equation of state,

$$(1) \qquad pv = R\theta,$$

in which p is the pressure, v the specific volume, i.e., the volume of 1 gram of gas, θ the absolute temperature (273° higher than the Celsius temperature ϑ), and

R a constant peculiar to the gas. The absolute temperature is

$$\theta = 273 + \vartheta. \tag{2}$$

This conception of absolute temperature is introduced in order to bring into use in calculations, in the most convenient way, the fact that, under constant pressure, when the temperature is raised 1° Cels., all gases expand 1/273 of the volume which they occupy at 0° Cels.

If a gas whose mass is M occupies the volume V its specific volume is

$$v = \frac{V}{M} \frac{\text{cm.}^3}{g}, \tag{3}$$

and its specific weight (the reciprocal of its specific volume) is

$$s = \frac{1}{v} = \frac{M}{V} \frac{g}{\text{cm.}^3}. \tag{3b}$$

From these we find

$$pV = R \,.\, M \,.\, \theta. \tag{4}$$

When we have one mol of gas, and m is its molecular weight, then

$$pvm = R \,.\, m \,.\, \theta,$$

$$\text{or} \quad pV_0 = R_0\theta. \tag{5}$$

Here $V_0 = vm$, the volume of 1 mol (or the molecular volume in cubic centimeters), and since, by Avagadro's and Gay-Lussac's law, this is the same for all

gases, under the same pressure and temperature, it follows that

$$R_0 = R \cdot m, \tag{6}$$

which has one and the same value for all gases.

R could be called the *specific*, and R_0 the *general*, gas constant.

These important constants can therefore be determined for any gas of known molecular weight, in any state, from its pressure, volume, and temperature. We choose 32 grams of oxygen in the standard state, and place its atomic weight at 16. Since the specific weight of oxygen is 0.00143 gr. cm.$^{-3}$, its molecular volume is

$$\frac{32}{0.00143} = 22400 \text{ c.cm.},$$

and this is the volume of one mol of any perfect gas. With $p = 1$ atmosphere $= 76 \times 13.596 = 1033.3$ g.*cm.^{2} and $\vartheta = 0°$ Cels. or $\theta = 273°$ Cels., it follows that

$$R_0 = \frac{1033.3 \times 22400}{273} = 84800 \frac{\text{g.*cm.}}{1° \text{ C.}} = 0.848 \frac{\text{kg.*m.}}{1° \text{ C.}}$$

$$= 832 \times 10^6 \text{ ergs}$$

$$= \frac{848}{432.5} \frac{\text{cals.}}{1° \text{C.}} = 1.96 \frac{\text{cals.}}{1° \text{C.}},$$

or $R_0 = 2$ cals., nearly.

To prove the proposition that R_0 has the same value for all gases in all states, we will calculate it for

saturated water vapor at 0°. Dieterici † gives for this case

$$p = 4.619 \text{ mm. Hg};$$

$$v = 204.680 \frac{\text{cdm.}}{g};$$

$$s = 4.8856 \frac{\text{mg.}}{\text{dm.}^3}.$$

We have then, since the molecular weight is 18,

$$R_0 = \frac{0.4619 \times 13.596 \times 204680 \times 18}{273} = 84750 \frac{\text{g*cm.}}{1^\circ \text{C}},$$

which corresponds closely with the calculated result given above.

With these few words of preparation we can now enter into the calculation of the changes of volume energy which take place in chemical reactions. If a substance gives off a small amount of gas, dV ccm., while the pressure (e.g., the atmospheric pressure) amounts to p dynes per square centimeter, then its intrinsic energy decreases by the amount necessary to overcome this pressure; that is, the intrinsic energy increased by the amount $-pdV$. The mechanical work that is developed by a chemical reaction, by which, under constant pressure, M grams of gas is formed, is therefore, by the equation of state of gases,

$$\int pdV = p\int dV = pV = R.M.\theta,$$

or the generation of 1 mol or m grams of gas is equal to $R_0\theta$.

† Wied. Ann. 38, 1889.

Just so often as, by the absolute temperature θ, one mol of gas is generated or dissipated at any unvarying constant pressure, just so often is the intrinsic energy of the substance decreased or increased by $R_0\theta$, i.e., by nearly 2θ calories (cals.).

This law makes it possible for us to determine the energy differences, without keeping the volume constant, by allowing the reaction to proceed under atmospheric pressure. If a reaction takes place, for example, a combustion under atmospheric pressure, and if the place of combustion is surrounded by a calorimeter, so that the gas escaping from it takes with it no more heat than is necessary to bring it to the same temperature as the outer air, then there will be work developed or used up by the air-pressure, and the differences of intrinsic energy will not come to observation as heat alone, but also as work, from which, however, in addition to the heat by the above law, we can calculate the energy differences. The heats of reactions by *constant pressure* are more often observed, and are of greater importance for practical use of the theory than those by constant volume—so much so indeed that it is customary to place them, instead of the others, in thermochemical equations. We find, for example, general data such as this:

$$\left\{\begin{array}{c} H_2 + O = (H_2O) + 68357 \text{ cals.} \\ \text{at } 18^\circ \text{ Cels., constant pressure of 1 atmosphere.} \end{array}\right\}$$

In this equation, however, the chemical symbols are used in still a third sense, besides the two already mentioned on pages 6 and 7.

There it was explained that the symbols mean molecular or atomic weights, when the equations in which they occur contain no values of energy; on the other hand, when these are present the symbols mean the amounts of intrinsic energy which the gram molecular or gram atomic weights contain. That, in the above equation, the symbols have a third meaning is apparent, for otherwise it would stand in contradiction to the one on page 16. What this third meaning, is can be shown in the following manner:

If E is the total intrinsic energy of the reacting substances in any moment of the chemical process, and p the pressure at the time; and if in an element of time the energy increases by the amount dE and the total volume by the amount dV, and the heat dQ is absorbed,—then, according to the principle of the conservation of energy,

$$dE = dQ - pdV.$$

If the volume does not change, then the heat absorbed is the differential of the heat of reaction Q_v, by constant volume, or

$$dE = dQ_v;$$

i.e., the difference of the intrinsic energies is measured by the heat developed, when the volume is constant. If, however, the volume changes (so that dV is no longer equal to zero), but the pressure p remains constant, then $pdV = d(Vp)$; therefore the differential of the heat of reaction Q_p by constant pressure satisfies the equation

$$d(E + pV) = dQ_p;$$

i.e., the development of heat by constant pressure measures the decrease that the quantity $E + pV$ suffers during the reaction: this we will call the *free energy by constant pressure*. It is the intrinsic energy increased by the product of pressure and volume.

The addition to the above equation of the words by "constant pressure" means, therefore, that by the chemical symbols we are to understand the free energy by constant pressure which the gram molecular or gram atomic weights contain. Since for one mol the product $pV = pvm = R\theta m = R_0\theta$, or nearly 2θ cals., the above equation is transformed, when the chemical symbols are to mean only the intrinsic energies contained in the mols, into the following form:

$$H_2 + 1 \,.\, R_0\theta + O + \tfrac{1}{2} \,.\, R_0\theta = (H_2O) + 68357 \text{ cals.};$$
$$H_2 + O = (H_2O) + 68357 - 1\tfrac{1}{2} \,.\, R_0\theta \text{ cals.};$$
$$H_2 + O = (H_2O) + 68357 - 1\tfrac{1}{2} \,.\, 2 \,.\, \theta \text{ cals.};$$
$$= (H_2O) + 67484 \text{ cal. at } 18^\circ \text{ Cels};$$

in which form it corresponds to the one given on page 16. One can transform, therefore, equations given "by constant pressure" into equations referring to intrinsic energies, by *adding* to the right side 2θ times the increase of gaseous mols which are formed during the reaction.

Upon the ground of the preceding explanation we will solve some of the problems for the case of constant pressure which were treated under constant volume.

Corresponding to the question treated on page 16, we will first calculate the heat that is developed when oxyhydrogen gas at ϑ° is transformed into liquid water

of the same temperature under constant pressure. We start from Thomsen's observation that
$H_2+O=(H_2O)+68357$ cals. at 18° Cels., 1 atmosphere, and use Regnault's results, under constant pressure;

$$\underset{\vartheta^\circ}{H_2} = \underset{18^\circ}{H_2} + 6.82(\vartheta - 18) \text{ const. pressure;}$$
$$\underset{\vartheta^\circ}{O} = \underset{18^\circ}{O} + 3.48(\vartheta - 18) \quad \text{“} \quad \text{“}$$

It follows then, as before, that

$$H_2+O=(H_2O)+68496-7.7\vartheta;\ \vartheta^\circ \text{ and } 1 \text{ atmosphere.}$$

Further, we can find, as we did on page 16, the heat which is developed when overheated steam at ϑ° is formed from oxyhydrogen gas at 0° and atmospheric pressure. We need for that the so-called total heat, λ, of steam, i.e., the heat that is necessary to change water at 0° into superheated steam at ϑ°, under constant pressure. According to Zeuner (and others) we have from Regnault's observations,*

$$\underset{\substack{\text{superheated}\\ \vartheta^\circ}}{H_2O} = \underset{0^\circ}{(H_2O)} + 18(606.5 + 0.305\vartheta^1 + 0.4805(\vartheta - \vartheta^1),$$

where ϑ^1 is the temperature of dry saturated vapor, at 100°, under same pressure. We obtain then

$$\underset{\substack{\text{superheated}\\ \vartheta^\circ}}{H_2O} = \underset{0^\circ}{(H_2O)} + 10602 + 8.649\vartheta, \text{ const. pressure.}$$

If we subtract this equation from

$$H_2 + O = (H_2O) + 68496 \left\{ \begin{matrix} 0^\circ \text{ Cels., 1 atmosphere} \\ \text{constant pressure} \end{matrix} \right\},$$

* According to Dieterici's measurements a few corrections are necessary. In place of 606.5 he finds 596.86.

we find

$$\underset{0^\circ}{H_2} + \underset{0^\circ}{O} = \underset{\text{superheated } \vartheta^\circ}{H_2O} + 57894 - 8.649\,\vartheta \left\{ \begin{matrix} \text{under constant} \\ \text{pressure of 1} \\ \text{atmosphere} \end{matrix} \right\}.$$

By this we obtain the answer to the following question: To what temperature could the oxyhydrogen flame, under atmospheric pressure, be brought, if by the combustion only overheated steam was formed and this did *not* again dissociate; and to what temperatures can the Regnault's constants be used?

The answer is

$$\vartheta = \frac{57894}{8.694} = 6700^\circ \text{ Cels.}$$

Since 100 grams of atmospheric air contains 23 grams of oxygen and 77 of nitrogen, or to 16 grams of oxygen in the air there are 53.6 grams of nitrogen, it is necessary that the 57894 calories (cals.) developed be used also to heat the nitrogen. The specific heat of N is 0.2438, so that under this condition the temperature of combustion, ϑ_1, of hydrogen in the air follows from equation

$$57894 = 8.649\vartheta_1 + 0.2438 \times 53.6\vartheta_1,$$

or

$$\vartheta_1 = 2700^\circ \text{ Cels.}*$$

How the difference between the heats of reaction under constant pressure and by volume is to be treated is well exemplified in the following examples.

---

* More complicated examples of this kind, especially those of technical importance, will be found in Naumann's Technisch-thermochemische Berechnungen zur Heizung, 1893.

A substance, any organic compound, containing C H, and O is combusted completely under constant atmospheric pressure. How can we find, from the observed heat of combustion V_p, the difference of the intrinsic energies of the compound and its combustion products? In other words, how can we find the heat of combustion V_v, at constant volume, that we would observe directly by the combustion of the compound, with the necessary amount of oxygen in a calorimetric bomb?

If the compound consists of

$$c \text{ atoms C, } h \text{ atoms H, and } o \text{ atoms O,}$$

then by the complete combustion we would obtain

$$c \text{ molecules } CO_2 \text{ and } \frac{h}{2} \text{ molecules } H_2O,$$

and for this there are necessary

$$2c + \frac{h}{2} - o \text{ atoms} = c + \frac{h}{4} - \frac{o}{2} \text{ molecules of } o.$$

The products of combustion must have cooled to the temperature of the room, about 17° Cels., before being removed from the calorimeter, which is the temperature at which the organic substance and oxygen were at first. Therefore for each molecule of the substance placed in the calorimeter c molecules come out as gas (CO_2) after the combustion, while $\left(c + \frac{h}{4} - \frac{o}{2}\right)$ of O as gas went in. If the combusted substance it-

self is solid or liquid, then by the combustion of one molecule a decrease of volume of

$$c - \left(c + \frac{h}{4} - \frac{o}{2}\right) = \frac{o}{2} - \frac{h}{4} \text{ molecular volumes}$$

is observed.

If, however, the substance is gaseous when placed in the bomb, then the increase of volume is

$$\frac{o}{2} - \frac{h}{4} - 1 \text{ molecular volumes.}$$

According to the law given on page 29 in the first case, which only will be treated here,

$$V_v = V_p + \left(\frac{o}{2} - \frac{h}{4}\right) . 2\theta \text{ cals.;}$$

or when the temperature is 17° Cels., or $\theta = 290°$, before and after the reaction, then

$$V_v = V_p + \left(\frac{o}{2} - \frac{h}{4}\right) . 580 \text{ cals.}$$

The energy equation corresponding would be

$$(C_cH_hO) + \left[2c + \frac{h}{2} - o\right] . O = c . CO_2 + \frac{h}{2}(H_2O) + V_v .$$

From the heat of combustion of a substance we can find easily the heat of formation, for if we first produce a substance from its elements and then combust it, it is no different from combusting its elements, in the proper amounts, directly. If we start from the equations

$$C + 2O = CO_2 + 97 \text{ Cals.,}$$
$$2H + O = (H_2O) + 68 \text{ Cals.,}$$

where the heat of formation is somewhat larger than Thomsen found it (see page 16), then the heat of formation, B_v, of the above organic compound, for constant volume, is given by the equation

$$B_v + V_v = 97c + 68 \cdot \frac{h}{2} \text{ Cals.}$$

The same heat, under constant pressure, B_p, is given by the equation (see page 31)

$$B_p + V_p = 97c + 68\frac{h}{2} + \frac{3h}{4} \cdot \frac{2\theta}{1000} \text{ Cals.},$$

or
$$B_p + V_p = 97c + 69\frac{h}{2} \text{ Cals.}$$

It follows, therefore, from the heat of combustion, under constant pressure, of raw sugar, $C_{12}H_{22}O_{11}$,

$$V_p = 1355 \text{ Cals.};$$

$$V_v = 1355 + \left(\frac{11}{2} - \frac{22}{4}\right) \cdot \frac{580}{1000} \text{ Cals.} = 1355 \text{ Cals.}$$

Julius Thomsen found that the vapor of acetic acid, $C_2H_4O_2$, when at a temperature of 7° under its boiling-point, 118°, would burn under atmospheric pressure, and would develop 227490 cals. per mol. When he calculated the molecular heat of the vapor at 23 cals., he found the heats of combustion at 118° and at 18° equal respectively to 227650 and 225350 cals. From this, it follows, that the heat of formation under constant pressure is

$$B_p = 97 \times 2 + 69 \times 2 - 225 = 107 \text{ Cals.},$$

and that for constant volume B_v is smaller by $\frac{4+2}{2} \times 2\theta$

-3.582 Cals. or 105 Cals. when the $C_2H_4O_2$ is liquid, and smaller by $\left(\frac{4+2}{2}-1\right)582 = 2.582$ Cals. or 106 Cals. when formed as a gas from its elements.

For ethyl alcohol, C_2H_6O, Julius Thomsen found, under constant pressure, the heat of combustion at the boiling-point, 78°.5, to be 341790 cals. The molecular heat is, according to Regnault, 20.8; therefore at 18° the heat of combustion $V_p = 340530$ cals. In the calorimetric bomb at 18°

$$V_v = 340530 + \left(\frac{1}{2} - \frac{6}{4}\right) 582 \text{ Cals.} = 340 \text{ Cals.}$$

Further, $B_p = 60$, and $B_v = 58$ Cals.

From the heat, observed by Stohmann, solid stearic acid, $C_{18}H_{36}O_2$, for constant volume gives 2707.1 Cals.; it follows, therefore, that under constant pressure, at 18°, the heat is 2711.8 Cals., and the heat of formation B_v is 263 Cals., and that of B is 258 Cals., when we calculate from the data given on page 36. Since Stohmann uses the heat of combustion of the diamond, 94 Cals., as that of carbon, and the same heat of combustion for hydrogen as we have used, viz., 69 Cals., he finds $B_p = 222.2$ Cals.

A coal contains $x\%$ of hydrogen; how much heat results from the compression, due to the complete combustion of the hydrogen with oxygen, while 1 gram of carbon burns?

Each gram of hydrogen requires $\frac{1}{4}$ mol of O, and causes when the water becomes fluid a compression of $\frac{1}{4}$ of a molecular volume, i.e., to formation of $\frac{1}{2} \cdot 2\theta = \frac{1}{4} \cdot 580$ cals. Each gram of coal causes therefore the

formation of $\frac{x}{100} \cdot \frac{580}{4} = 1.45x$ cals., an amount which is insignificant beside the 8000 cals. which one gram of carbon develops. Therefore calorimetric experiments on coals can be carried on at constant volume as well as under constant pressure without perceptibly changing the results.

In conclusion, it will be well to compare a few good measurements of the heat of explosion of oxyhydrogen gas under constant pressure in order to be able to judge of the degree of accuracy which has been reached. Measurements of this mixture have been made more often, and perhaps more accurately, than those of any other substance. J. Thomsen found by three experiments, made in the same manner, H_2O being taken as equal in molecular weight to 18,

68388, 68467, 68231 cals.,

the mean being 68357 cals.

Other good observers have found

68433, 68924 cals.

The combustions at constant volume when recalculated to constant pressure give still greater results; for example, Berthelot found in this way

69200 cals.

In comparing results it is well to observe which calorie and which molecular weight has been used. For H = 1.0025, O = 16, Thomsen's mean value becomes 68376 cals.; for H = 1, O = 15.96, it becomes, however, 68205 cals.

Compounds.	Heat of Formation. Intrinsic Energy of the Elements Minus that of the Compound. E_0	Heat of Solution in Water.	Heat of Combustion under Constant Pressure. V_p
Hydrochloric acid, HCl	220	173	....
Hydriodic acid, HI	−60	192	....
Water, H_2O	684	....	....
Sulphuretted hydrogen, H_2S	(30)	46	1367
Ammonia, NH_3	119	84	....
Ammonium chloride, NH_4Cl	758	−39	....
Carbon dioxide, CO_2	970	....	....
Sulphur trioxide, SO_3	1032	392	....
Sulphuric acid, H_2SO_4	1929	179	....
Potassium chloride, KCl	1056	−44	....
Sodium chloride, NaCl	977	−12	....
" hydroxide, NaOH	1019	99	....
" oxide, Na_2O	1002	550	....
" sulphate, Na_2SO_4	3286	5	....
" " $Na_2SO_4+10H_2O$	3478	−188	....
" carbonate, Na_2CO_3	2726	56	....
Zinc sulphate, $ZnSO_4+7H_2O$	2527	−43	....
Copper sulphate, $CuSO_4+H_2O$	1890	93	....
" " $CuSO_4$	1826	158	....
" " $CuSO_4+5H_2O$	2011	−27	....
Methane, CH_4	212	....	2119
Ethane, C_2H_6	274	....	3704
Benzene, C_6H_6	−137	....	7994
Ethylene, C_2H_4	−33	....	3334
Methyl alcohol, CH_3OH	506	....	1822
Ethyl alcohol, C_2H_5OH	570	....	3405
Acetic acid, CH_3COOH	1041	....	2254

The preceding small table is condensed from J. Thomsen and others,* and will be found useful for practice and comparison.

The values are given in Ostwald calories, and most are taken from the observations and calculations of J. Thomsen. They are all given for the temperature of 18° Cels., and 1 atmosphere pressure.

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*J. Thomsen, Thermochemische Untersuchungen. Ostwald Lehrbuch d. allg. Chem. 2 ed., II, i, 1893. (Leipzig.) Stohmann, Die Verbrennungswärmen organischer Verbindungen, Zeit. f. phys. Chem. 6, 1890.

PART II.

ENTROPY.

CHAPTER I.

THE FACTORS OF ENERGY.

In Part I two forms of energy were considered—that of heat and that of volume. They were, however, investigated in different ways. The energy of heat was more completely treated than that of volume, which appeared only as a correction to the measurement of heat. Notwithstanding this, however, we are better acquainted with the ways of the energy of volume than with that of heat. If, in order to show this difference, we assume that the intrinsic energy of a body changes only by the gain or loss of heat, and by the increase or decrease of volume; and if we call the change, during the time dt, of intrinsic energy dE, and the increase of heat dQ, and that of work, by change in volume, dA, —then

$$dE = dQ + dA.$$

Since we know, further, that

$$dA = -pdV,$$

we need only a knowledge of dQ to understand the equation fully. We arrive at this by the following analogy between the different forms of energy. First, we will consider more exactly the physical nature of p and V.

Let us imagine a closed cylinder in which a piston K can be moved, on both sides of which is a liquid or gaseous body which can increase or decrease its intrinsic energy by changes of volume. We will assume that on the one side the pressure is p_1 and the volume is V_1, while on the other it is p_2 and V_2. It is then plain that a change of intrinsic energy can only occur by the decrease or increase of volume energy when p_1 is $\gtrless p_2$. If p_1 is $> p_2$, then the energy of the body which is under the greater pressure increases by $-p_1 dV_1$ (decreases in reality), and the other by $-p_2 dV_2$. Here $dV_1 = -dV_2$, for the one volume increases by the amount by which the other decreases for the sum of the two volumes, i.e., the volume of the cylinder remains unchanged. Further, the greater pressure, p_1, decreases, while the lesser, p_2, increases. We can represent it by assuming that each body has the tendency to come to a lower pressure, and the greater tendency overcomes the other.

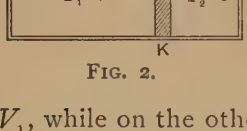


FIG. 2.

From this method of considering the question we obtain the following results:

The *first* condition that causes the intrinsic energy of a body to change, by increase or decrease of volume energy, is the possibility of a change in its volume. If this changes, then the volume of another body must of

necessity change also, but the sum of the volumes which are considered can never change.

The *second* condition that causes the intrinsic energy of a body to change, by increase or decrease of volume energy, is the inequality of pressure in the different bodies. By this each body shows a tendency, which increases with the pressure, to diminish its pressure, so that, during the change, the greater ones decrease while the smaller ones increase; or, in short, the volume energy is transformed from a higher to a lower pressure.

It is self-evident that these conditions are not confined to the problem just considered of the closed cylinder, but are equally applicable to all change of volume.

The sense of this treatment can be perhaps better understood in the form given by Poincaré. If, in an isolated system, i e., in a system in which only an exchange of energy between the constituents is possible, after any process, nothing is changed but the pressure and volume of its two constituents, then the higher pressure has certainly decreased, while the lower has increased.

In general, it is possible to show that the change of intrinsic energy in every form is a product, IdM, where I has the same meaning as the pressure in volume energy, and M that of volume, in volume energy. I is called the *intensity* of the form of energy, and M, according to Helm, the *quantity* of the form of energy, or, according to Ostwald, the *capacity* of the body for that form of energy.

By the transformation of the above considerations for volume energy to heat energy, it is to be observed that the entrance to the knowledge of the former is won in an entirely different manner than to that of the latter. In the volume energy we have the volume in tangible form, also the pressure, and from the two we can find the energy; that is, from M and I we can find E.

By heat, however, it is different. Here by our organs of sensation we have something that corresponds exactly to pressure. We need only, in the above second condition, to replace the word pressure by temperature, volume energy by heat energy, to obtain the fundamental equation of heat energy. Further, in the course of the historical development of the phenomena of heat, the theory has been built up from experimental facts, so that here we are confronted by the problem of how to find the function M from I and E.

It is well to start from the fact that from the volume energy A and the pressure p we can find the function V; that is,

$$-dV = \frac{dA}{p}.$$

But here there is a difficulty that must not be overlooked. If the volume of a body increases by dV, then the intrinsic energy changes in a different manner, according to the way in which the volume increases. If it is very slow—as is the case when the internal pressure is but slightly greater than the outer, and just enough to increase the volume—then the body goes over into another state from that which it

would assume were the change sudden, as is the case when the difference of external and internal pressure is large. Then the single molecules of the expanding body are in violent motion and kinetic energy is liberated, which is gradually turned into heat by the friction. It is only after the disappearance of this heat that the body reaches the same final state as it does when the expansion is gradual.

If we call the increase of energy that takes place by the gradual increase of volume dV, d_0E, and that by the sudden increase by the same amount dV, d_kE, and if we call the kinetic energy developed in the latter case dK then

$$d_kE = d_0E + dK,$$

or

$$d_kE > d_0E, \quad \frac{d_kE}{p} > \frac{d_0E}{p}.$$

According to the equation above,

$$\frac{d_0E}{p} = -dV,$$

and

$$\frac{d_kE}{p} = -dV_k;$$

then

$$-dV_k = -dV + \frac{dK}{p}.$$

Thus, for a sudden change of volume, we have

$$-dV < -dV_k,$$

or

$$-dV_k > \frac{d_0E}{p}, \quad d_0E < -pdV_k;$$

and only when $dk = 0$ do we have

$$-dV = -dV_k,$$

or

$$-dV_k = \frac{d_0E}{p}, \quad d_0E = -pdV_k.$$

According to this, condition *one* (page 42), does not hold for $-V_k$, i.e., the sum of all values of this function, that belong to the bodies under consideration, is not unchangeable, but rather increases steadily. On the other hand, $-V_k$, as $-V$, is a function fully determined by the momentary state of the body (as are all internal motions), and not dependent on the manner of the change from one to the other.

Thus in the study of the phenomena of heat we are in the position just described; i.e., the states into which a body comes, after absorption of the same amount of heat, are different according as the reaction goes slowly or rapidly. According to a method of consideration which will be developed later, these two reactions are distinguished as reversible and non-reversible; but we cannot draw out the difference of energy in any other form than that which the slow process develops. While, in the above case, $d_kE - d_0E$ appears as kinetic energy of the particles of the body and can be measured as heat, and d_0E appears as volume energy; in the case that heat is supplied, no such distinction is possible.

We would expect, in the case of heat energy, the amount of heat, dQ, supplied to a body at temperature θ is comparable to the volume energy d_0E, that is supplied at pressure p, that is,

$$dQ \leqq \theta dS,$$

where the function S, comparable to $-V_k$, is a quantity peculiar to that state of the body, and which has the principal property that the sum of all the terms S can never decrease.

In order to prove the correctness of this proposition, founded on analogy, it is necessary to follow a train of thought that was proposed by Sadi Carnot, the so-called cycle. The exact study of this method, however, presupposes a knowledge of the properties of perfect gases, so, in our next chapter, we will consider this important question.

CHAPTER II.

THE THERMODYNAMICS OF PERFECT GASES.

LET the intrinsic energy of 1 gram of any substance vary by de, while at the same time the amount of heat dq is supplied and the mechanical work da is done from the outside (as, *e.g.*, by the atmospheric pressure). Then, according to the principle of the conservation of energy, for every possible change of the sort we have

$$de = dq + da;$$

and since $da = -pdv$,

$$de = dq - pdv, \tag{1}$$

Here we must remember that no form of energy, especially kinetic energy, arises during the change, except those named, i.e., we assume that the change takes place very slowly. We will first assume that the amount of heat $d_v q$ is supplied to the body, while we hold the volume constant, by which the absolute temperature θ is increased by $d\theta$, and the pressure p by dp; the intrinsic energy then increases by

$$d_v e = d_v q = c_v d\theta, \tag{1a}$$

where c_v is the specific heat by constant volume, that is, the heat which is necessary to raise 1 gram of the

substance 1° Cels. when its volume is not allowed to change. Secondly, we will assume another amount of heat, $d_\theta q$, to be supplied, keeping at the same time the temperature constant; this process will change, generally, the volume energy of the substance, and so it will expand as well as change its internal structure. By the Mariotte–Gay-Lussac law, however, we have the equation of state,

$$pv = R\theta, \tag{2}$$

and from this we see that the intrinsic energy changes only with the temperature—a proposition which has been proven experimentally with gases. We place, in accordance with this, the change in the intrinsic energy, by constant temperature, equal to zero; therefore

$$d_\theta q = pdv. \tag{3}$$

If the two changes, which we have considered separately, follow one another, then the intrinsic energy, of the gram of substance considered, changes by

$$de = d_v e + d_\theta e = c_v d\theta = d_v q + d_\theta q - pdv. \tag{1b}$$

Now of the second change; up to the present, we have only determined that it shall take place at constant temperature, or isothermally, but have not given the limits of the pressure and volume at which we shall stop the reaction. We will now assume that the pressure in the second change decreases just so much as it increased by the first change. Then the total change which the gas has undergone has not changed its final

pressure, and the total addition of heat can be represented by the specific heat of the gas under constant pressure; that is,

$$d_v q + d_\theta q = c_p d\theta. \tag{4}$$

In connection with (1*b*) we have, therefore,

$$(c_p - c_v)d\theta = pdv. \tag{5}$$

From (2), however, by differentiating, we find

$$pdv + vdp = Rd\theta; \tag{2b}$$

or, since by constant pressure, $dp = 0$,

$$pdv = Rd\theta,$$

and from (5)

$$c_p - c_v = R. \tag{6}$$

After completing the proof in this way—by assuming that the difference between the specific heats is unvarying, for substances which follow the Mariotte–Gay-Lussac law, and whose intrinsic energy changes only with the temperature—we are further in the position to prove the law by which the state of a gas changes when no heat energy, but only volume energy, is applied.

From (1*b*)

$$d_q e = -pdv = c_v d\theta, \tag{7}$$

and from (2) and (6) it follows that

$$pdv + vdp = (c_p - c_v)d\theta. \tag{8}$$

The elimination of $d\theta$ leads to the relation between changes of pressure and of volume. As long as only

volume energy is added to or removed from the gas, then

$$vdp = -\frac{c_p}{c_v} pdv;$$

$$\frac{dp}{p} + \frac{c_p}{c_v} \cdot \frac{dv}{v} = 0. \tag{9}$$

We call this change of state—which takes place without any change in the heat energy—adiabatic. For isothermal changes we have from (2*b*), where $d\theta = 0$,

$$\frac{dp}{p} + \frac{dv}{v} = 0. \tag{10}$$

The integral of this equation, it is self-evident by (2), is

$$pv = R\theta_0 = p_0 v_0, \tag{11}$$

where p_0, v_0, and θ_0 mean respectively the pressure, specific volume, and temperature in the initial state of the isothermally changed gas. While we can thus easily integrate (10), it is more difficult to integrate (9). We can only do so when we know more of the relation of the specific heats $\frac{c_p}{c_v} = x$. For gases, within certain limits, this proportion is constant, i.e., by equation (6), the two specific heats c_p and c_v themselves are constant. So far as this, the integral of equation (9) is

$$pv^x = p_0 v_0^x, \quad x = \frac{c_p}{c_v}; \tag{12}$$

and with the aid of (7) and (8) it follows, further,

$$\left.\begin{aligned} \theta v^{x-1} &= \theta_0 v_0^{x-1} \\ \theta p^{\frac{1}{x}-1} &= \theta_0 p_0^{\frac{1}{x}-1} \end{aligned}\right\}. \tag{12b}$$

The proportion x of the specific heats is for perfect gases about 1.41. Finally, the integral for (7) is

$$e = e_0 + c_v\theta, \tag{13}$$

which shows how the intrinsic energy of a gram of gas changes with the temperature; e_0 is an integration constant peculiar to each gas.

We must not forget, however, the conditions under which these equations were developed. We have assumed that there are in Nature perfect gases which have the following three properties: (1) They follow the Mariotte–Gay-Lussac law; (2) their specific heats are unvarying; (3) their intrinsic energies do not change when the temperature does not.

The meaning of equations (12) and (12*b*) can be made clear by a simple example. If a gas is adiabatically compressed to the five-hundredth part of its volume, the temperature rises from the initial one of 17° Cels., or 290° absolute, to 2700°, as the substitution of $v = \frac{1}{500}v_0$, $\theta_0 = 290$, $x = 1.41$ shows. The pressure rises by it to $500^{1.41}$ or to 6400 times its initial value. If, on the contrary, the pressure is adiabatically raised to 500 times its initial value, then the temperature is raised to 1500°.

For the following, it is important to show graphically the formulæ (11) and (12) for isothermal and adiabatic changes of pressure and volume. Let us

imagine in a cylinder, whose axis has the direction v, one gram of gas. In the co-ordinate system let the volumes be represented by the abscissæ, and the pressures, which correspond to these volumes, by the ordinates. Starting from any initial state, the point (v, p) traverses two curves according as it is an isothermal or an adiabatic. The curves are always different, since c_p, according to (6), cannot be equal to c_v. If we do not supply heat, then the curve followed is an *adiabatic;* if its intrinsic energy is unchanged, at the same time supplying heat and volume energy, then, according to (13), it is an isothermal. (Fig. 3.)

Each point (v, p) of the diagram represents a possi-

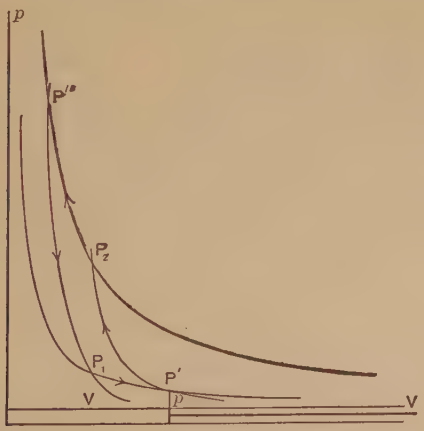


FIG. 3.

ble state of the gas. Conversely, each possible state of the gas is shown by the point (v, p). The temperature, by (2), is also determinable. We see from this that the change from any state P_1 of a perfect gas

into any other state P_2, can be shown by a system of curves that is composed of the isothermal of the one state, and the adiabatic of the other. We have only to follow these curves to their point of intersection P', whose co-ordinates (v', p') satisfy at the same time the equation of the isothermal through P_1 and the adiabatic through P_2,

$$p'v' = p_1v_1, \quad p'v'^{\varkappa} = p_2v_2^{\varkappa},$$

and it follows

$$(14) \qquad \left(\frac{v'}{v_1}\right)^R = \left(\frac{p_2}{p_1}\right)^{c_v}\left(\frac{v_2}{v_1}\right)^{c_p}, \quad \left(\frac{p'}{p_1}\right)^R = \left(\frac{p_1}{p_2}\right)^{c_v}\left(\frac{v_1}{v_2}\right)^{c_p}.$$

The change of the gas, shown by the series of points $P_1P'P_2$, takes it from the one state into the other.

Finally, these considerations allow us to find the heat which is necessary for this transformation. The isothermal supply of heat given by (3) is

$$(15) \qquad d_\theta q = pdv = \frac{R\theta_1}{v}dv;$$

by integration we have

$$(15b) \qquad q_{P_1P'} = R\theta_1 l\frac{v'}{v_1}.$$

The adiabatic supply of heat is 0; the total supply of heat is therefore

$$q_{1.2} = R\theta_1 l\frac{v'}{v_1} = \theta_1 l\left(\frac{p_2}{p_1}\right)^{c_v}\left(\frac{v_2}{v_1}\right)^{c_p}.$$

$$(16) \qquad q_{1.2} = \theta_1\left\{c_v l\frac{p_2}{p_1} + c_p l\frac{v_2}{v_1}\right\}.$$

If this gives the heat necessary for the isothermal change P_1P' and the adiabatic $P'P_2$; then, by the simple exchange of the indices 1 and 2, we can find the heat necessary to go from 2 to 1 on the isothermal of 2 and the adiabatic of 1, i.e., through the series of points $P_2P''P'$. We obtain

$$(16b)\quad q_{2.1} = \theta_2 \left\{ c_v l\frac{p_1}{p_2} + c_p l\frac{v_1}{v_2} \right\} = -\theta_2 \left\{ c_v l\frac{p_2}{p_1} + c_p l\frac{v_2}{v_1} \right\}$$

$$(17)\quad \frac{q_{1.2}}{\theta_1} + \frac{q_{2.1}}{\theta_2} = 0.$$

CHAPTER III.

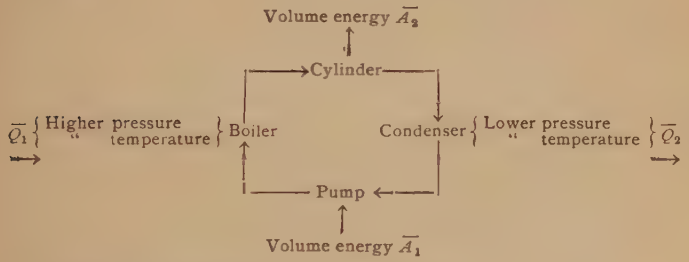
THE CYCLE.

TECHNICAL experience led Sadi Carnot (1824) to the method—the cycle—by which he was able to make clear the relation between heat and temperature.

Saturated vapor that produces work, in a steam-engine, does it by going from the high temperature and pressure of the boiler, to the low temperature and pressure of the condenser. The working body therefore is in a different state after doing the work, than it was before, so that, for the theory of the process, we must consider not only the heat taken and given up in the boiler and condenser, and the work done in the cylinder, but we must also take account of the change in the intrinsic energy of the steam itself. The consideration of the latter, however, can be neglected when we make use of a process by which, as before, a transformation of energy takes place, but in which the working body is finally in the same state as it was in the beginning. In a steam-engine, this can be fulfilled by bringing the steam and condensed water back again into the boiler by means of a pump (which must perform work, since the steam is to be brought from a lower to a higher pressure); they will then attain the

higher temperature in the boiler. The volume energy set free in the cylinder, which is produced at the cost of the pressure and temperature, will be greater than that supplied to the pump only by the volume energy necessary for increasing the pressure.

The scheme for a steam-engine whose steam completes such a cycle, i.e., where after the end of the process the steam contains the same energy as before, will be



Or shorter, according to C. Neumann,

$$\overline{A_2} - \overline{A_1} = \overline{Q}$$

Higher temp. $\overline{Q_1}$ —— $\overline{Q_2}$ Lower temp. Process $\overline{K}$.

and according to the principle of the conservation of energy,

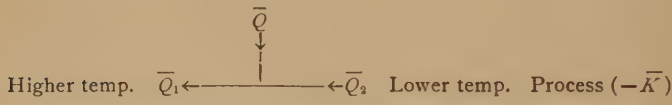
$$\overline{Q_1} = \overline{Q} + \overline{Q_2}, \tag{1}$$

i.e., while from the energy applied, $\overline{Q_1}$, the amount $\overline{Q_2}$ goes over as heat to the foreign body, and the amount $\overline{Q_1} - \overline{Q_2}$ is transformed into the work $\overline{A_2} - \overline{A_1}$.

The change of energy which takes place during a cycle can always be brought to the form of scheme $\overline{K}$. Often the single separable parts do not occur in

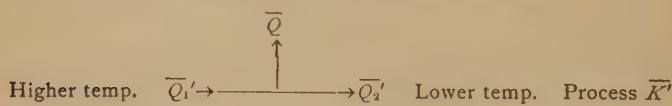
different places, as here, in the boiler and cylinder, etc. The complete technical steam-engine, however, divides the natural process in just the way that we must do, in our development of the theory.

We will now assume—and that is the principal point in Carnot's train of thought—that the process can also take place in the reverse order, i.e., by reversing all the arrows in the scheme we will still have a possible natural process, that is;

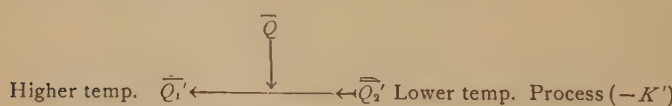


Here the heat $\overline{Q_1}$ can be found from the heat $\overline{Q_2}$ by the aid of the volume energy $\overline{Q}$.

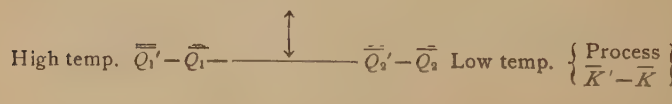
When now another natural process, that takes place between the same temperatures, is followed until the same amount $\overline{Q} = \overline{Q_1} - \overline{Q_2}$ of heat is transformed into volume energy, then the scheme will be



And if reversible,



If we follow process $\overline{K}'$ by process $(-\overline{K}')$, we will have


High temp. $\overline{\overline{Q_1}}' - \overline{\overline{Q_1}}$ $\overline{\overline{Q_2}}' - \overline{\overline{Q_2}}$ Low temp. $\left\{\begin{matrix}\text{Process} \\ \overline{K}' - \overline{K}\end{matrix}\right\}$

i.e., a simple exchange of heat, equal to

$$\overline{Q_1'} - \overline{Q_1} = \overline{Q_2'} - \overline{Q_2},$$

from a higher to a lower temperature. In the same way the arrangement $(\overline{K} - \overline{K_1})$ gives us

which, as before, is a simple exchange of heat, $\overline{Q_1} - \overline{Q_1'} = \overline{Q_2} - \overline{Q_2'}$ from a higher to a lower temperature.

According to Carnot's theorem, which, on page 44, we considered as self-evident: *Pure exchanges of heat can only take place from a higher to a lower temperature; or heat has a tendency to go from higher to lower temperatures.* From this it follows that

$$\overline{Q_2'} - \overline{Q_2} \geqq 0, \qquad \overline{Q_2'} \geqq \overline{Q_2}, \tag{2}$$

when the process $(\overline{K'} - \overline{K})$ is possible, i.e., when $\overline{K}$ is reversible. If both processes, $\overline{K}$ and $\overline{K'}$, are reversible, we have, further,

$$\overline{Q_2} - \overline{Q_2'} \geqq 0, \qquad \overline{Q_2} \geqq Q_2',$$

which is only possible, in view of the former equation, when

$$\overline{Q_2'} = \overline{Q_2} \tag{2b}$$

For the expression of our result it is sufficient that $\overline{Q_2}$ and $\overline{Q_2'}$ are amounts of heat which are given out by the same transformation of energy $\overline{Q}$. If, however, we bring the result of our train of thought into the form

$$\frac{\overline{Q_2'}}{\overline{Q}} \geqq \frac{\overline{Q_2}}{\overline{Q}} \tag{3}$$

according as $\left\{\begin{array}{c}\overline{K}\text{ alone}\\ \text{or}\\ \overline{K}\text{ as well as }\overline{K}'\end{array}\right\}$ is reversible, then we obtain the law: *The proportion of the exchanged heat to that transformed is the same by all reversible processes, which take place between the same limits of temperature; and is greater by all non-reversible processes between the same limits.*

By aid of (1) it follows from (3) that

$$\frac{\overline{Q_1'}}{\overline{Q}} \gtrless \frac{\overline{Q_1}}{\overline{Q}} \tag{3b}$$

All reversible processes, that take place between the same limits of temperature, need equal supplies of heat to transform equal amounts of heat energy, and all non-reversible ones need greater amounts.

If we once determine this proportion for *one* reversible process, then it is determined, for the same interval of temperature, for all. We can find this for a gas, provided that the gas behaves like a perfect one during all the changes under which it is considered. We must especially ascertain here that the proportion is determined during an interval of temperature inside of which it acts like a perfect gas. This condition is satisfied, however, by the two changes considered on pages 53 and 54, from any one state to any other, by a Carnot cycle.

They are also reversible processes, since all amounts of heat given up must be by infinitely small differences of temperature, and all changes of volume energy by infinitely small differences of pressure, if the process is to go in the manner described.

The total amount of heat, $\overline{Q}$, transformed in the above we will now designate by $q_{12} + q_{21}$ in each cycle, and place it equal to Q. Then

$$q_{12} + q_{21} = Q = \overline{Q}. \tag{4}$$

The heat q_{12}, applied at the higher temperature, that we have called $\overline{Q}_1$, we will now designate by Q_1, and that amount at the lower temperature, q_{21}, formerly $\overline{Q}_2$, we will term Q_2.

$$q_{12} = Q_1 = \overline{Q}_1, \quad q_{21} = Q_2 = -\overline{Q}_2. \tag{5}$$

The equation on page 55, (17), then takes the form

$$\frac{Q - Q_2}{\theta_1} + \frac{Q_2}{\theta_2} = 0, \quad \frac{Q_1}{\theta} + \frac{Q - Q_1}{\theta_2} = 0;$$

from which it follows

$$\frac{Q}{-Q_2} = \frac{\theta_1 - \theta_2}{\theta_2}, \quad \frac{Q}{Q_1} = \frac{\theta_1 - \theta_2}{\theta_1}. \tag{6}$$

From (3), then, we have for all general processes

$$\frac{Q}{-Q_2} \leq \frac{\theta_1 - \theta_2}{\theta_2} \text{ when } \left\{ \begin{matrix} \text{non-reversible} \\ \text{reversible} \end{matrix} \right\}. \tag{7}$$

The ratio of the transformed heat, to that given off at the lower temperature is, at greatest, equal to the ratio of the difference of temperature, to the lower temperature.

Further, we have

$$\frac{Q}{Q_1} \leq \frac{\theta_1 - \theta_2}{\theta_1}. \tag{7b}$$

The ratio of the transformed heat to that absorbed is, at greatest, equal to the ratio of the difference of temperature, to the temperature at which it is taken up.

For example, if a steam-engine works with a boiler-pressure of six atmospheres and a condenser-pressure of one-half atmosphere, then the temperature at which the heat is absorbed, according to the table for the tension of steam, is 159° Cels. or 432° absolute, and the temperature at which the heat is given up is 46° Cels. or 319° absolute: the difference of temperature is then 113°. Therefore, no machine with such a difference of temperature can transform more than 113/319 of the heat given up in the condenser into work, or more than 113/432 of that absorbed by the boiler.

With the assistance of (1), it follows from (7) that

$$(8) \qquad \frac{Q_1}{\theta_1} + \frac{Q_2}{\theta_2} \leqq 0 \text{ for } \left\{ \begin{matrix} \text{non-reversible} \\ \text{reversible} \end{matrix} \right\} \text{ cycles.}$$

This relation holds for every cycle, by which the amounts of heat Q_1 and Q_2 have been absorbed at the temperature θ_1 and θ_2 respectively, if no other change of heat has taken place. From the conception of the cycle it follows that the total amount of heat absorbed, $Q_1 + Q_2 = Q$, is equal to the amount of the other energy which is given off, no matter which, θ_1 or θ_2, is the higher temperature.

The case of a body going from a state 1 to another state 2, in a way not consisting of adiabatics or isothermals, can now be made clear. For this purpose it is necessary to complete the change of state, by an isothermal going through 1 and an adiabatic going

through 2, to a cycle $12P'1$, and to cause the parts $2P'$ and $P'1$ to take place reversibly, so that the whole process is reversible or not according as 12 is or not (Fig. 4). Then we must draw through the separate points of the line 12 adiabatics, e.g., through the points a, b, c the adiabatics aa', bb', cc'. In this way we divide the cycle into many single ones, as $abb'a'a$, $bcc'b'b$, each of

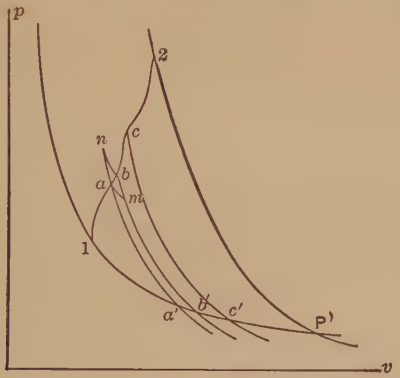


FIG. 4.

which will be the more exactly fulfilled by Carnot's cycle, the nearer the points a, b, c, etc., are together. For example, $abb'a'a$ lies between the Carnot cycles $amb'a'a$ and $nbb'a'n$ when am and nb' are isothermals. These Carnot cycles are in general reversible if the process 12 is reversible.

If we call Q_{12} the heat that is supplied in the transformation 12, and Q^*_{12} that supplied for reversible Carnot cycles, i.e., those consisting of adiabatics and isothermals, then the heat belonging to one division ab of the line 12 is dQ_{12}, and that to the division $b'a'$ is dQ^*_{21} or $-dQ^*_{12}$. Since now dQ_{12} is enclosed between

the amounts of heat which correspond to the isothermals *am* and *nb*, then for each process, as *abb'a'a*, if it is a reversible process, according to (8), we have

$$\frac{dQ_{21}}{\theta} - \frac{dQ^*_{12}}{\theta_1} = 0,$$

and for all single processes, or for the total process $12P'1$,

$$\int \frac{dQ_{12}}{\theta} \leq \frac{Q^*_{12}}{\theta_1}, \tag{9}$$

according as it is a non-reversible or a reversible process, by which formulæ the integral is to be taken in the way that the state 1 is transformed into 2. Whichever way we use, for the change of state (1, 2), the expression

$$\int \frac{dQ_{12}}{\theta} \quad \text{or} \quad \int_1^2 \frac{dQ}{\theta}$$

will always have the same value for reversible processes (as by the Carnot method), and smaller values for every other that is not reversible.

This fact leads us to the simplest mathematical expression of the formula, in that we make use of the function S, for which each body, in a certain state, has a certain value, according as to what arbitrary value we give to S for any standard state of the body. If we give, for example, a point in the field (v, p) of a possible state, designated by 0, the value S_0, and the points 1, 2, 3, etc., the values S_1 S_2, . . . which are given by the equations

$$S_1 - S_0 = \int_0^1 \frac{dQ}{\theta}, \quad S_2 - S_0 = \int_0^2 \frac{dQ}{\theta}, \ldots$$

then

$$\int_1^2 \frac{dQ}{\theta} = S_2 - S_1 \tag{10a}$$

for reversible changes; or in general,

$$\int_1^2 \frac{dQ}{\theta} \leqq S_2 - S_1 . \tag{10}$$

Finally, for an infinitely small change of state we have

$$dQ \leqq \theta dS. \tag{11}$$

This function S is, as the intrinsic energy, determinable only to an arbitrary constant S_0. It was called by *Clausius* the entropy. We can prove by this our assumption (page 46) that S has the property by which it, as well as $-V_k$, can never decrease. We imagine every possible change of energy divided into a transformation of energy, that takes place in a body, and a transmission of energy, unchanged, from one body to another: then it is easy to see that by each change of energy, in which heat comes into play, we will have an increase of entropy for the body which absorbs heat, and a decrease for the one which gives it up. That the first is in the preponderance is shown by (11), from Carnot's principle, which gives heat the tendency to go from higher to lower temperatures. For if a body absorbs the heat

$$dQ' \leqq \theta dS,$$

another must give it up. For this absorption of heat however, the equation

$$dQ' \leqq \theta' dS'$$

holds, in which $dQ' = -dQ$.

If by dZ we understand the increase of entropy that takes place by the transformation of heat,

$$dZ = dS + dS',$$

it follows that

$$dZ \geqq \frac{dQ}{\theta} + \frac{dQ'}{\theta'}$$

or

$$dZ \geqq dQ\left(\frac{1}{\theta} - \frac{1}{\theta'}\right).$$

According to the law of intensity, $\theta' \geqq \theta$, therefore, dZ can never be negative.

(12) $$dS + dS' \geqq 0.$$

If a system has completed a cycle, its entropy, by (10), need not increase. Since, in the interior of the system, the transmission of heat cannot lead to a decrease of the entropy (12), but is open to an increase, the entropy taken up from the outside during the cycle can well be negative. but never positive (Poincaré).

It is worthy of notice, further, that when an adiabatic takes place reversibly, the entropy does not change, as is shown by

$$dQ = \theta dS$$

when

$$dQ = 0.$$

CHAPTER IV.

THE ENTROPY OF GASES AND GAS MIXTURES.

THE function called entropy is known to us for perfect gases. The formula (16), on page 54, gives the heat which is necessary for a Carnot reversible change of state for 1 gram of gas. This function, which is, as before mentioned, determinable only to a constant (page 65), is

$$(1) \qquad s_2 - s_1 = c_v l\frac{p_2}{p_1} + c_p l\frac{v_2}{v_1},$$

where s_1 and s_2 are the values of s for 1 gram of gas in the states 1 and 2. The function (s) is therefore

$$(2a) \qquad \left\{ \begin{array}{l} s = s_0 + c_v lp + c_p lv, \\ ds = \dfrac{c_v dp}{p} + \dfrac{c_p dv}{v}, \end{array} \right\}$$

where s_0 is the arbitrary constant. From the equation of state for a gram of gas

$$(3) \qquad pv = R\theta. \qquad \text{where } R = c_p - c_v, \quad (3b)$$

we have

$$(2b) \qquad s = s_0 + Rlv + c_v l(\theta R) = s_0' + Rlv + c_v l\theta$$

$$(2c) \qquad s = s_0 + Rlp + c_p l(\theta R) = s_0'' - Rlp + c_p l\theta,$$

where s' and s_0'' are again constants.

The entropy of M grams of gas can be found by multiplying (2*a*), (2*b*), and (2*c*) by M; and that for 1 mol by multiplying by m, when m is the molecular weight of the gas.

Let us now imagine in the volume V, at the temperature ϑ, or the absolute temperature $\theta = 273 + \vartheta$, a number of different gaseous bodies, which can be regarded as perfect gases; and let us further assume that we have the masses, of the single chemically different gases, equal to

$$M_1 = n_1 m_1, \quad M_2 = n_2 m_2, \quad \ldots, \tag{4}$$

where m_1, m_2, ... are the molecular weights of the different gases, and $n_1, n_2, \ldots$ the number of mols of each gas present. Further, that $R_1, R_2, \ldots$ are the gas constants, and the terms $p_1, p_2, p_3, \ldots$ of the formulæ

$$p_1 V = n_1 m_1 R_1 \theta, \quad p_2 V = n_2 m_2 R_2 \theta, \ldots \tag{5}$$

are the *partial pressures* of the gaseous constituents.

From Avogadro's Law, pages 25 and 26, we have

$$m_1 R_1 = m_2 R_2 = \ldots = R_0 = 84800 \text{ g.*cm.} : {}^\circ C. = 2 \text{ cals.} \tag{6}$$

From (5) with the aid of (6) we then have

$$PV = NR_0\theta = (M_1 R_1 + M_2 R_2 + \ldots)\theta, \tag{7}$$

where

$$P = p_1 + p_2 + \ldots, \tag{8a}$$

$$N = n_1 + n_2 + \ldots \tag{8b}$$

Since N is the total number of mols in the mixture, NR_0 is the gas constant for the same, and P is the total pressure.

We divide (5) by (7) and obtain

$$(9) \qquad \frac{p_1}{P} = \frac{n_1}{N} = C_1, \quad \frac{p_2}{P} = \frac{n_2}{N} = C_2, \ldots,$$

where C_1, C_2, ... are the *concentrations** of the single constituents of the mixture. It is to be observed from (8) and (9) that

$$(10) \qquad C_1 + C_2 + \ldots = 1.$$

The specific volumes of the constituents are

$$(11) \; v_1 = \frac{V}{M_1} = \frac{R_1\theta}{p_1} = \frac{R_0\theta}{m_1 p_1} = \frac{R_0\theta}{m_1 C_1 P}, \quad v_2 = \frac{R_0\theta}{m_2 C_2 P}, \ldots;$$

and the volume of each mol of the single members is

$$(12) \qquad m_1 v_1 = \frac{R_0\theta}{P} \cdot \frac{1}{C_1}, \quad m_2 v_2 = \frac{R_0\theta}{P} \cdot \frac{1}{C_2}, \ldots$$

With the help of this formula it is possible to bring the expression for the entropy of the constituents into a different form. The entropy s_1 of the unit of mass of the first constituent is then, by (2*b*) and (11),

$$s_1 = s_{01} + R_1 l \frac{R_0\theta}{m_1 C_1 P} + c_v l R_1 \theta,$$

and this formula is, by (6) and (3*b*), transformed into

$$(13) \qquad \begin{aligned} s_1 &= [s_{01} + c_{\cdot 1} l R_1] + c_{p_1} l\theta - R_1 lP - R_1 lC_1 \\ &= s_{01} + c_{p_1} l R\theta - R_1 lP - R_1 lC_1. \end{aligned}$$

One mol of the first constituent possesses, then, the entropy

$$(13b) \; \begin{aligned} m_1 s_1 &= [m_1 s_{01} + m_1 c_{p_1} l R_1] + m_1 c_{p_1} l\theta - R_0 lP - R_0 lC_1 \\ &= m_1 s_{01} + m_1 c_{p_1} l R_1 \theta - R_0 lP - R_0 lC_1. \end{aligned}$$

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* Plank, Weid. Ann. 32, 1887; see also the reference on page 11.

The expression in the bracket can be regarded as a new constant, as was the quantity s_0 earlier.

From (2*b*) and (11) it follows, further,

$$s_1 = s_{01} + R_1 l\frac{V}{M_1} + C_{v_1} l\theta R_1$$

$$= s_{01} + R_1 lV + c_{v_1} l\theta R_1 - R_1 lM_1 \tag{14}$$

$$= m_1 s_1 = m_1 s_{01} + R_0 lv + m_1 c_v l\theta R - R_0 lM_1. \tag{14b}$$

In all cases in which the entropy of the whole system is the sum of the entropies of its constituents, we obtain from (13*b*) and (9) the total entropy. Thus

$$S = S_0 + [n_1 m_1 c_{p_1} + n_2 m_2 c_{p_2} + \dots] l\theta - R_0 [n_1 lp_1 + n_2 lp_2 + \dots].$$

$$S = S_0 + C l\theta - R_0 l(p_1^{n_1}, p_2^{n_2} \dots). \tag{15}$$

It is self-evident that the total entropy is the sum of the entropies of the constituents, only when the mixing is a reversible process. The simplest case of application, i.e., when all constituents are alike and present in the same amounts, in (15), leads to direct contradiction to (2*c*), as Gibbs has already observed and C. Neumann* lately reiterated.

If we assume k constituents, then

$$n_1 = n_2 = \dots = \frac{1}{k} N,$$

and from (9)

$$p_1 = p_2 = \dots \frac{1}{k} P,$$

and from (15)

$$S = S_0 + C_p l\theta - R_0 N l\frac{P}{k}$$

Leipzig, Ber., 1891.

while from (2c) we obtain

$$S = S_0 + c_v l\theta - R_0 N l P.$$

We see from this that this method of consideration, that each of the like particles fill the volume V with the partial pressure $\frac{P}{k}$, is apparently wrong. But we can account for it, for here we have a mixture of like particles which is not reversible, as a mixture of unlike ones would be, and therefore the conditions of development are not fulfilled.

If, on the other hand, we imagine the mixture of like particles to be made in the usual way, so that all parts are under the common pressure P, and each fills the kth part of the volume V, then the process is a reversible one.

CHAPTER V.

THE RELATIONS BETWEEN HEAT AND VOLUME ENERGY.

THE principal mathematical result of the investigation begun on page 41 is a more complete method of expression of the principle of the conservation of energy.

(1) $$dE = dQ + dA.$$

This equation indicates that a body, during the time dt, has had (positive or negative) heat or work (dQ and dA) applied to it; and that their sum is the increase of intrinsic energy. If the work dA is done only by the change of volume, under the influence of the outer pressure (e.g., of the atmosphere) p, then

(2) $$dA = -pdV.$$

We know further, however, from a previous chapter, that

(3) $$dQ \leqq \theta dS,$$

where θ is the absolute temperature and S the entropy, and we also know that S is a function of a body, just as its volume is, and that is known.

From this the principle of the conservation of energy assumes the form

(4) $$dE \leqq \theta dS - pdV.$$

It is important here to keep the fact clear that dE, dS, and dV represent very various changes, namely, all those infinitely small changes that are possible under the condition, that only gain or loss of heat and of volume energy can take place.

We could, for example, let S, V, and E represent co-ordinates, so that all states (that could occur by reversible processes, i.e., those to which the equation

$$dE = \theta dS - p dV \tag{5}$$

would correspond) can be regarded as points on a surface, whose tangential planes are determined, in each point given, by the co-ordinates S, V, and E, by the aid of θ and p. In this way we can readily understand that from any state there are many changes possible; for example, one by $dS = 0$, but dV not equal to 0; another by $dS = dV$, etc.

Among other things, equation (4) shows us that the entropy can never decrease by any change by which the volume energy and intrinsic energy remain unchanged, for from $dE = 0$, $dV = 0$, it follows that $0 \leqq dS$.

The laws which concern constant volume are similar to those for constant temperature or pressure. We obtain them by transformation of (4):

$$dE \leqq d(\theta S) - S d\theta - p dV.$$

$$d(E - \theta S) \leqq - S d\theta - p dV. \tag{6}$$

$$dE \leqq d(\theta S) - d(pV) - S d\theta + V dp.$$

$$d(E - \theta S + pV) \leqq - S d\theta + V dp. \tag{7}$$

The function $E + pV$ has already been introduced on page 30.

Equation (6) shows us that by isothermal processes, by which the volume is not changed, the function $E - \theta S$ cannot increase; while (7) shows that in isothermal processes, by which the pressure cannot increase, another function, $E - \theta S + pV$, cannot increase. The function $E - \theta S$ is called the *thermodynamical potential* by constant volume, or also the *free energy* by constant temperature. Corresponding to this, $E - \theta S + pV$ is called the *thermodynamical potential* by constant pressure, or the *free energy* by constant pressure and temperature.

The usefulness of these functions for the mathematical treatment of chemical processes has been shown by the numerous and careful investigations of Duhem.*

The much-combated so-called "third principle of thermodynamics" of Berthelot† (the two others express the laws of energy), according to which a chemical reaction strives to form substances by which the most heat is developed, has theoretically no foundation, and has shown itself to be of no practical value. The laws just derived must take its place, especially the law which is so similar, $dS \geqq 0$. This law has, however, already been applied to chemical processes by Horstmann.

We will apply equation (4), as we did in a previous

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* Duhem, Le potential thermodynamique (Paris, 1886); and since in numerous articles, especially in the Traveaux et mémoires des facultés de Lille, 1–5, III, 11, 12, 13.

† Essai de mécanique Chimique (Paris, 1879).

chapter, to the case that the substance considered is present in two different states; and that the amount of substance in the one state can, by transformation from the other, be increased, and *vice versa*. For example, formula (4), applied to a mixture of water and ice, will express the changes of energy for the transformation of a small amount of water into the solid state, or, conversely, those by the melting of a small amount of ice to water. It will be well now to develop this formula (4), for the case of a system where the constituents are in the state of exchange, from the formulæ of the two single constituents.

We make use of the name as proposed by *Gibbs* of *phases* to distinguish the states in which the substance is present.

The single homogeneous bodies of a system we will call their phases, in so far as their possible changes consist of an exchange of substance; or in so far as not to regard the quantity and form of these bodies. According to this, water and ice are to be considered as two phases of the same substance. Accordingly, we will designate two bodies as *phases of one and the same substance* when, to their possible changes, the sum of the increase of mass is equal to zero, i.e., the one increases by just so much as the other decreases. Therefore, states of aggregation, states of dissociation, allotropic and isomeric modifications, are to be looked upon as phases of one and the same substance.

Let us now assume that the intrinsic energies of two phases of the same substance, for whose changes we wish to find the formulæ, are E_1 and E_2; that the en-

tropies are S_1 and S_2; the volumes V_1 and V_2; the masses M_1 and M_2; the temperatures θ_1 and θ_2; and the pressures p_1 and p_2.* Each of the phases (water and ice) is a body that can absorb or give up the heat energy θdS and the volume energy $-pdV$, but each is capable of another change. Its energy can increase in such a way that its mass increases. Other changes of energy. as electrical, etc., we will not consider here.

We have

$$(8) \qquad \left\{ \begin{aligned} dE_1 &\leqq \theta_1 dS_1 - p_1 dV_1 + \Pi_1 dM_1, \\ dE_2 &\leqq \theta_2 dS_2 - p_2 dV_2 + \Pi_2 dM_2, \end{aligned} \right\}$$

where $\Pi_1 = \dfrac{\partial E_1}{\partial M_1}$, or the increase of energy by the reversible increase of the unit of mass, when it takes place without change of heat or volume energy. These equations would also hold if the two phases were separated, so that no exchange of energy could take place. We will, however, turn our attention now to changes that take place during an exchange of energy. Among all the possible changes for which the above equations hold, there are also such by which no supply of energy from outside and no loss of energy from inside, i.e., no internal change of energy, takes place ; but the system is *isolated*, as in the case of equilibrium. For such systems we have the condition

$$(9) \qquad dE_1 + dE_2 = 0, \quad dE_2 = -dE_1;$$

* These quantities are not completely independent of one another, e.g., the specific gravity gives a relation between M, V, θ, and p.

that is, the amount of energy of the system suffers no change. Then only an exchange from one to the other of the phases is possible. Further, for the internal changes, we have the condition

$$(10) \qquad dM_1 + dM_2 = 0, \quad dM_2 = -dM_1;$$

that is, that the mass of the system is constant. Further,

$$(11) \qquad dV_1 + dV_2 = 0, \quad dV_2 = -dV_1,$$

for a change in the volume filled by the system is only possible by increase or decrease of volume energy. In a corresponding way it follows, finally, when all exchange of heat between two phases is reversible, that

$$(12) \qquad dS_1 + dS_2 = 0, \quad dS_2 = -dS_1,$$

because reversible entropy changes of the system have the same meaning as increase or decrease of heat. According to experience, it is only possible for a system to have a reversible exchange of heat when the temperature and pressure have become equalized. By (8), by addition, it follows

$$(13) \quad 0 \leqq (\theta_1 - \theta_2)dS_1 - (p_1 - p_2)dV_1 + (\Pi_1 - \Pi_2)dM_1.$$

When pressure and temperature have become equalized, then

$$(14) \qquad \theta_1 = \theta_2, \quad p_1 = p_2$$

or

$$(15) \qquad 0 \leqq 0 \,.\, dS_1 - 0dV + (\Pi_1 - \Pi_2)dM_1.$$

Since now a possible change of a system is an

increase or decrease of the mass of a phase, then $dM_1 \gtrless 0$, and from (15)

$$\Pi_1 = \Pi_2. \tag{16}$$

This holds with the exception of the case when one of the two phases does not exist, but whose formation is possible. For then only an increase of mass is possible, or $dM_1 > 0$; and so from (15) we have

$$\Pi_1 \geqq \Pi_2. \tag{16b}$$

The function Π, whose absolute mass, according to (8), is the square of a velocity (cm. : sec.)^2, obtains from this very great importance; it is called by *Gibbs* the *potential* of the substance. Since later the word potential is used in another sense, we will call Π the *chemical intensity** of the substance, in keeping with the analogy between Π and p and θ. As the pressure and temperature, so the chemical intensity of phases in contact becomes equalized.

We can now express our results in the following manner: When, after entrance of equilibrium of temperature and pressure in an isolated system, consisting of two phases of the same substance, changes (of temperature and pressure) are still possible, by which one or the other of the phases increase, *then both phases have same chemical intensity*; if, however, only one phase is present, then the other can only appear when it has *not a smaller chemical intensity* than the other.

* This term is only proposed as a temporary name. By deeper mathematical knowledge of chemical phenomena Π will undoubtedly be called by its old and proper name, affinity.

In conclusion, it is easy from (8) to deduce (4), which holds for the system as a whole. Equation (4) holds for the changes of a system that consists of the change of the total heat or volume energy. Increase or decrease of mass are alone excepted, therefore

$$dM_1 + dM_2 = 0. \tag{17}$$

If the exchange of mass in the system is reversible, then

$$\Pi_1 = \Pi_2. \tag{18}$$

Temperature and pressure are also equalized, or

$$\theta_1 = \theta_2 = \theta, \quad p_1 = p_2 = p. \tag{19}$$

Then follows, by addition of (8),

$$dE \leqq \theta dS - p dV,$$

where E, S, and V are the energy, entropy, and volume of the entire system, and the lower sign (=) holds when the total heat and volume energy only undergo a reversible change.

a. Isothermal Change in a System of Two Phases of the Same Substance.

We will now find the heat which is necessary to transform one phase, into another of the same substance, which is in contact with it, *when during the transformation neither the temperature nor the pressure changes, and the process is reversible.*

We will call a transformation reversible when the supply of a certain amount of heat transforms just as

great an amount of phase 1 into phase 2 as will be formed of phase 1 from phase 2 by the removal of the same amount of heat.

In order to bring the constancy of temperature to a simple expression, we turn to equation (6) on page 73, where we have the differential of the temperature. We have, therefore, for a reversible change,

$$(1) \qquad -d(E - \theta S) = Sd\theta + pdV.$$

If we now consider θ and V as independent variables, upon which all the others in the equation depend, as on page 73 (where they were the co-ordinates of a point, so that the value of the thermodynamical potential $(E - \theta S)$ is represented by a point on a curved surface), then S and p are negative partial differentials of this function with respect to θ and v respectively. Or

$$(2) \qquad \frac{\partial S}{\partial V} = \frac{\partial p}{\partial \theta}.$$

Now we can calculate the heat dQ, which is added to the intrinsic energy of the system by an infinitely small change of state. If θ and v are increased by an infinitely small amount, then the intrinsic energy will be increased by

$$(3). \qquad dE = \theta dS - pdV = dQ + dA,$$

and the energy which appears as heat will be

$$4) \qquad dQ = \theta dS = \theta\left(\frac{\partial S}{\partial \theta}d\theta + \frac{\partial S}{\partial V}dV\right);$$

or when the process takes place isothermally, i.e., $d\theta = 0$,

$$dQ = \theta dS = \theta \frac{\partial S}{\partial V} dV, \tag{5}$$

or from (2)

$$dQ = \theta dS = \theta \frac{\partial p}{\partial \theta} dV. \tag{6}$$

Since, however, it was provided that during the process the pressure does not change (as if, e.g., the process takes place under atmospheric pressure), then p is not dependent upon V; no matter how much heat is supplied isothermatically, or how much of one phase is transformed into the other, the pressure remains the same. The pressure, however, can depend upon the temperature, i.e, an isothermal process by another temperature is only possible under another pressure.

From these considerations we can go from infinitely small changes of volume and heat directly over to finite ones. We then have

$$\Delta Q = \theta . \frac{dp}{\partial \theta} . \Delta V; \tag{7}$$

i.e., in order to bring about a volume increase ΔV, in a system of two phases of the same substance, by the reversible transformation of one phase into the other, by constant pressure and temperature, we must supply the amount of heat equal to ΔQ. This amount of heat is proportional to the change of volume caused by it, as well as to the absolute temperature of the process, and finally to the quantity $\frac{\partial p}{\partial \theta}$, which depends

upon the influence of the pressure p upon the temperature θ of the transformation.

This law was developed essentially by Clapeyron in 1834, and can be regarded as the most important result of the mechanical theory of heat in its old form of development.

The increase of intrinsic energy during the volume increase ΔV follows from (3) and (7) as

$$(8) \qquad \Delta E = \theta \frac{\partial p}{\partial \theta} \Delta V - p \Delta V = \theta^2 \frac{\partial}{\partial \theta} \left(\frac{p}{\theta} \right) . \Delta V.$$

Particularly important for the knowledge of the amounts of heat ΔQ is the quantity $\frac{\partial p}{\partial \theta}$, a differential that we can understand better when p, as a function of θ, is graphically produced.

We can readily see then that for each temperature θ a value of the differential corresponds. The curve which shows the relation between p and θ is called the *tension* curve of the system of two phases considered.

b. Changes in the State of Aggregation.

The melting of ice and the freezing of water are reversible processes to which we can apply our general results. Since ice, by melting, decreases its specific volume or increases its specific weight, ΔQ and ΔV in this case have different signs; therefore $\frac{\partial p}{\partial \theta}$ is negative, and the melting-point sinks by increasing pressure. This consequence was found, from the mechanical

theory of heat, by J. Thomsen in 1850, and proven experimentally later by W. Thomson and others.

To show how the units of mass are to be treated, we will now find the value of the differential $\frac{\partial p}{\partial \theta}$. If we express the energy by g.*cm., then 1 gram of ice takes up 79.87 cals. of heat-energy, or

$$\Delta Q = 79.87 \times 43250 \text{ g.*cm.}$$

The specific gravity of ice is 0.918, the specific volume therefore 1.09, while the specific volume of water at 0° does not differ from 1 except in the fourth decimal place. Therefore we must substitute, for ΔV, -0.09 cm.³, and it follows that

$$\frac{dp}{\partial \theta} = \frac{79.87 \times 43250}{273 \cdot (-0.09)} = -140_{000} \frac{\text{g.*}}{\text{cm.}^2 \,^\circ \text{C.}}$$

When the pressure increases by 140 kg.*cm.², the melting-point is lowered 1°, or one atmosphere increase of pressure lowers the melting-temperature by 0.0074° Cels.

From the heats of solution for 1 gram of solid and fluid acetic acid, -40.80 and $+5.58$ cals. respectively, we find the heat of melting to be 46.42 cals. The increase of volume by the melting of one gram is 0.1595 cm.³; therefore we have (Visser)

$$\frac{\Delta V}{\Delta Q} = 0.003436 \frac{\text{cm.}^3}{\text{cals.}} = \frac{0.003436}{43250} \cdot \frac{\text{cm.}^3}{\text{g*}}.$$

Since the melting-point is 16.6°,

$$\frac{d\theta}{dp} = \frac{(273 + 16.6)0.003436}{43250} 1033.3 = 0.0238 \frac{^\circ \text{C.}}{\text{atmospheres}},$$

while from observation the increase of temperature by an increase of pressure of one atmosphere is 0.02435° Cels.

Evaporation is also a reversible isothermal process and so must be considered here. Since the tensions corresponding to the different boiling-temperatures are easy to observe (i.e., p is easily found experimentally from θ), equation (7) will prove valuable for the determination of the increase of the specific volume by evaporation.

From the table of Zeuner, derived from Reginault's observations, the function $\frac{\partial p}{\partial \theta}$ has, for water at 100° Cels. or $\theta = 373°$, the value 2.72, expressed in centimeters of a column of mercury; therefore

$$\frac{\partial p}{\partial \theta} = 2.72 \times 13.6 \frac{\text{g.*}}{\text{cm.}^2 \, ^\circ \text{C.}}.$$

Since, further, the heat of evaporation of one gram of water at 100° Cels. is, according to Regnault, 536.5 cals., with Joule's equivalent of heat we have

$$\Delta V = \frac{536.54 \times 2400}{373 \times 2.72 \times 13.6} = 1649 \text{ cm.}^3.$$

This calculation is in Zeuner's table for water from $-20°$ to 200° Cels., and also for a number of other liquids, investigated by Regnault. If we calculate the specific volume of steam at 100°, under the assumption that it follows the Mariotte–Gay-Lussac law, we find (page 26) 1701 ccm.g.

By formula (7) we can also treat cases of sublimation, where the solid substance goes directly over into the gaseous state. If we distinguish the three states of aggregation by the indices 1, 2, and 3, and the transformations between them by double indices, then we have the relation

$$(9)\quad \left\{ \begin{array}{c} \Delta Q_{12} = \theta\left(\frac{\partial p}{\partial \theta}\right)_{12} \cdot \Delta V_{12}, \quad \Delta Q_{23} = \theta\left(\frac{\partial p}{\partial \theta}\right)_{23} \cdot \Delta V_{23}, \\ \Delta Q_{31} = \theta\left(\frac{\partial p}{\partial \theta}\right)_{31} \cdot \Delta V_{31}, \end{array} \right\}$$

when all the processes take place at the same temperature θ, reversibly and by constant pressure. From the law of the conservation of energy it then follows that

$$\Delta Q_{12} + \Delta Q_{23} = \Delta Q_{13},$$

or

$$(10)\qquad \Delta Q_{12} + \Delta Q_{23} + \Delta Q_{31} = 0.$$

For the change of volume we have

$$(11)\qquad \Delta V_{12} + \Delta V_{23} + \Delta V_{31} = 0.$$

If we substitute in (10) the values from (9), we obtain

$$(12)\quad \left(\frac{\partial p}{\partial \theta}\right)_{12} \cdot \Delta V_{12} + \left(\frac{\partial p}{\partial \theta}\right)_{23} \cdot \Delta V_{23} + \left(\frac{\partial p}{\partial \theta}\right)_{31} \cdot \Delta V_{31} = 0.$$

And from (11) and (12)

$$(13)\quad \Delta V_{12} : \Delta V_{23} : \Delta V_{31} = \left(\frac{\partial p}{\partial \theta}\right)_{23} - \left(\frac{\partial p}{\partial \theta}\right)_{31} : \left(\frac{\partial p}{\partial \theta}\right)_{31} - \left(\frac{\partial p}{\partial \theta}\right)_{12} : \left(\frac{\partial p}{\partial \theta}\right)_{12} - \left(\frac{\partial p}{\partial \theta}\right)_{23}.$$

Since $\frac{\partial p}{\partial \theta}$ is the slope of the tangent of the angle which the tension curve forms at the point considered with the θ axis, and can be considered as the (negative) slope of the tension curve, equation (13) can be expressed in words as follows: When three tension curves meet in one point (θ, p), the increase of the specific volume by the increase of one such state, is proportional to the difference of slope of the other two.

In all substances the increase of volume ΔV_{12} by melting is small, generally very small, as against that by evaporation or sublimation; therefore it meets the curves for the two latter at a small angle. For water, by which ΔV_{12} is negative, the sublimation curve at the melting-point is steeper than that for evaporation.

According to Dieterici's results for water at 0° Cels. or 273° absolute temperature,

$$\Delta Q_{23} = 596.8,\ \Delta Q_{12} = 79.87 \text{ cals.} \therefore \Delta Q_{13} = 676.67.$$

From this it follows, when the pressure is expressed in millimeters of a column of mercury,

$$\left(\frac{\partial p}{\partial \theta}\right)_{23} = 0.3398, \qquad \left(\frac{\partial p}{\partial \theta}\right)_{13} = 0.3852,$$

or

$$\left(\frac{\partial p}{\partial \theta}\right)_{23} = 0.4619 \frac{\text{g.*}}{\text{cm.}^2\,^\circ\text{C.}}, \quad \left(\frac{\partial p}{\partial \theta}\right)_{13} = 0.5238 \frac{\text{g.*}}{\text{cm.}^2\,^\circ\text{C.}}.$$

By which the specific volume of steam at 0° Cels. is 204680 cm.^{3}g. (and the mechanical equivalent of heat $= 432.5$). ΔV_{12} is smaller than 2.10^{-6} times ΔV_{13}; therefore $\left(\frac{\partial p}{\partial \theta}\right)_{12}$, shown graphically, does not differ

from ∞. Fig. 5 shows an approximate picture of these relations. The curves shown, that intersect at melting-point $\theta = 273°$ ($p = 4.62$ mm. of a column of mercury) represent the tension or limiting curves of

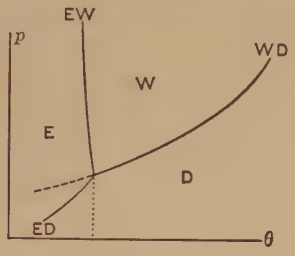

FIG. 5.

the three states of aggregation. In these curves the function V of θ and p (as well as of the intrinsic energies) is discrete.

If we lay out, from the single points (θ, p) of the plane, the corresponding values of V as perpendiculars to the plane, we obtain a surface that consists of three wings which are independent of one another; they correspond to the solid (E), liquid (W), and gaseous (D) states of water.

The well-known phenomenon of the "overcooling" of water, by which the fluid state is retained below 273° absolute temperature, but which cannot be reversibly transformed into the solid state, reminds us that our results are only true when we consider reversible changes in the state of aggregation.

By equation (16*b*), (page 78,) we can conclude at least, from the fact of "overcooling," that the chemical intensity of the ice produced is not smaller than

that of the water from which it is formed. Concentrated solutions fulfil equation (7), not only with respect to evaporation and freezing, but also to crystallization from the solution, in so far as it is an isothermally reversible process.

c. Allotropic Changes.

The transformation from one allotropic state to another takes place, in many cases, isothermally and reversibly, just as with the case of a transformation between two states of aggregation. Such changes are called by O. Lehmann enantiotropic, in contrast to monotropic, which take place only in one, and not in the reverse, state, as explosive processes.

The change from rhombic to monoclinic sulphur takes place reversibly at 95.6° Cels. Addition of heat increases the monoclinic modification, and decrease of heat the rhombic. Here we have, therefore, a case in which we can use equation (7); it was proven by van't Hoff* from observations by Reicher. From these observations, $\Delta Q = 2.520$ Cals., $\Delta V = 0.014$ ccm. for one gram of sulphur; it therefore follows that

$$\frac{\partial\theta}{\partial p} = \frac{(273 + 95.6)0.014}{2.520 \cdot 43250} = 0.000047 \frac{^\circ \text{C. cm.}^3}{\text{g.}^*};$$

i.e., the temperature of the transformation increases by 0.05° Cels., when the pressure is increased by one atmosphere, which agrees with our experience.

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* van't Hoff, Études de dynamique chimique (Amsterdam, 1884).

d. Dissociation.

The volatilization of ammonium chloride must, although it appears to be only a change of the state of aggregation, be looked upon as a decomposition of the compound NH_4Cl into NH_3 and HCl; because by the molecular weight, 53.5, the vapor tension should be 1.85, while at the temperature of 350° Cels. it is approximately 1. The complete decomposition of the NH_4Cl would lead to the vapor tension 0.92, which lies near to the values observed at high temperatures.

Such a partial decomposition of a substance, which depends on the temperature, is known as dissociation when, as here, it takes place reversibly. Since 1857, when Sainte-Claire Deville discovered this phenomenon in steam and showed its great importance, we have been able to bring many long-known processes, as the above, under its heading

Dissociation is to be looked upon as an analogous process to evaporation; for, as by the latter, we find also by dissociation a certain pressure by a certain temperature in a closed space. If we increase the space in which the substance is confined without changing the temperature, the dissociation increases; if, however, we decrease the volume, the products of dissociation unite again, so that certain dissociation pressure is always present for that one temperature. For example, the dissociation tensions for NH_4Cl are (Horstmann):

at	200°	260°	300°	360°	
	1.4	6.9	25.9	77.8	cms. of mercury.

There is, therefore, a curve for the dissociation tension, and the application of equation (7) is clearly apparent.

From the numerous cases in which the liberation of the water of crystallization can be considered as a phenomenon of dissociation, we will consider only the one observed by G. Wiedemann, which shows the dependence of the dissociation tension of zinc sulphate, $ZnSO_4.7H_2O$ upon the temperature:

at ϑ =	22°	30°	40°	50°	60°	70	78.8°	88° Cels.
p =	1.97	3.15	5.49	9.29	14.88	23.3	33.78	48.67 cms. Hg.

The reversibility, of the process is, however, a necessary condition to the application of the theory. That calcite at 450° C. gives off CO_2 is a well-known instance of dissociation; the tension curve for which is given (Le Chatelier) as follows:

at ϑ =	547°	610°	625°	740°	745°	810°	812°	865° Cels.
p =	27	46	56	255	289	678	753	1333 mms. Hg.

The chemically analogous case of the decomposition of manganese carbonate is, however, to be excluded here (Ostwald), for the product manganous oxide and the CO_2 are reduced according to the formula

$$3MnO + CO_2 = Mn_3O_4 + CO,$$

and the process is therefore not reversible.

If the dissociation consists in the liberation of gaseous constituents from the solid or liquid substance, and if, further, the assumption that the liberated gases follow the equation of state for a perfect gas is allow-

able, then equation (7) becomes essentially transformed. As the increase of volume we can then take the volume of the gas liberated, neglecting the volume that the substance occupies when in the solid or fluid state. Since now the volume of a molecule of a perfect gas is, at absolute temperature θ and under pressure p, according to (5), (page 25), equal to $R_0\theta/p$; then the heat Q_0, according to (7), which must be supplied for the formation of 1 mol of gas is

$$Q_0 = \theta\frac{\partial p}{\partial \theta}\frac{R_0\theta}{p} = R_0\theta^2\frac{\partial lp}{\partial \theta}. \tag{14}$$

According to (8) the corresponding change of intrinsic energy is

$$E_0 = R_0\theta^2\frac{\partial lp}{\partial \theta} - R_0\theta = R_0\theta^2\left(\frac{\partial lp}{\partial \theta} - \frac{\partial l\theta}{\partial \theta}\right) \tag{15a}$$

$$= R_0\theta^2\frac{\partial}{\partial \theta}l\left(\frac{p}{\theta}\right)$$

$$E_0 = -R_0\theta^2\frac{\partial lv}{\partial \theta}. \tag{15b}$$

Here v is the specific volume of the gas, and R_0 is equal (nearly) to 2 cals. (page 27).

Horstmann applied (4), among other things, to the absorption of ammonia by silver chloride. The compounds AgCl, $2AgCl3.NH_3$, and $AgCl.3NH_3$ react towards ammonia as does a substance towards its vapor, in that by the pressure of ammonia beside silver chloride, in a closed space, the ammonia is absorbed until a certain pressure, depending on the temperature, is reached.

For example, at 12° Cels. the pressure is 3.2 cms. of mercury, and this pressure by further addition of ammonia remains unchanged. When so much ammonia has been absorbed that the compound $2AgCl.3NH_3$ is formed, further addition of ammonia raises the pressure to 52.0 cms. of mercury, and this remains constant until the compound $AgCl.3NH_3$ is formed. From the observations of the dissociation tension of these compounds. namely,

at	8°	12°	16° Cels.
$p =$	43.2	52.0	65.3 cms. of Hg

it follows that for 12° the differential quotient $\frac{\partial p}{\partial \theta} = 2.76$*. On the other hand, it follows from the

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* Since it is often necessary in physical-chemical calculations to ascertain differential quotients from a table, the appended formula is given. If we know the pressure p from w to w (as from 4 to 4) degrees, that is, for θ, $\theta \pm w$, $\theta \pm 2w$, etc., and seek for θ the differential quotient $\frac{\partial p}{\partial \theta}$, we form a table of differences, then the differences of these differences, etc., and so calculate finally the arithmetical mean of the first and third of these differences that are on either side of θ. If these means are $f'(\theta)$, $f'''(\theta)$, etc., then

$$\frac{\partial p}{\partial \theta} = \frac{1}{w}\left\{f'(\theta) - \frac{1}{6}f'''(\theta) + \frac{1}{30}f'''''(\theta) - \ldots\right\}.$$

In our example the differences are 8.8 and 13.3, whose arithmetical mean is 11.05; if we now substitute this in the formula for $f'(\theta)$, we obtain,

$$\frac{\partial p}{\partial \theta} = \frac{1}{4}\left\{11.05\right\} = 2.76.$$

TRANS.

observation that to remove one molecule of NH_3 the heat $\Delta Q = 9500$ cals. is necessary, from (14),

$$\frac{\partial p}{\partial \theta} = \frac{9500 \times 52.0}{2 \times 285^2} = 3.04 \text{ cms. Hg.}$$

That the two results do not agree can be accounted for partly by the errors of observation, and partly by the use of (14) instead of (7); i.e., by the assumption that the liberated ammonia acts as a perfect gas.

The relations, as expressed by (7) and (14), between the tension curve of a reversible chemical process; the heat necessary for the completion of this process; and the changes of density corresponding to them; are particularly fitted for the drawing of conclusions from phenomena which take place at very high or very low temperatures and pressures.

We do not always need a supply of heat for the formation of substances of greater specific volume, or finally for its transformation into gaseous form. For only when p is an increasing function of θ does positive ΔV follow from positive ΔQ. The dissociation curves for cyanogen, CN–CN, and for acetylene, C_2H_2, probably, partly rise and partly fall (Ostwald). While both substances are unstable at red heat, the first forms in the blast-furnace, and the other in the electric arc. It is therefore not to be assumed that all substances on the sun are dissociated into their elements; that would be true only for those whose dissociation tensions, even at higher temperatures, increase with the temperature.

e. The Heat of Solution and Dilution.

Equation (15*a*), (page 91,) can be applied to still another process which led to a law derived by Kirchhoff which is famous as being the first application of the principles of thermodynamics to chemical processes.

In order to evaporate 1 mol of pure water we need an amount of energy, at the temperature θ and the vapor tension P_0, equal to

$$E_0 = R_0\theta^2 \frac{\partial}{\partial\theta} l\left(\frac{P_0}{\theta}\right).$$

In order to evaporate the same amount of water from a solution of a salt, we need another amount of energy at same temperature θ and vapor tension (smaller) P, equal to

$$E = R_0\theta^2 \frac{\partial}{\partial\theta} l\left(\frac{P}{\theta}\right).$$

Since in both cases 1 mol of pure steam is formed (we assume here that the substance in solution is not volatile to any great degree), then $E - E_0$ is the difference of energy of 1 mol of pure water and 18 rams of the solution. If de is the amount of energy which we must supply to 18 grams of the salt solution, together with the addition of dN mols of water in order to keep the temperature at θ, then

$$de + EdN = E_0 dN$$

must be true, for the two sides give the difference of energy for the liquid and gaseous amounts of water dN,

The negative heat of dilution de for the amount dN is therefore

$$de = -R_0\theta^2 \frac{\partial}{\partial\theta} l\frac{P}{P_0} \cdot dN = -R\theta^2 \frac{\partial}{\partial\theta} l\frac{P}{P} \cdot dM,$$

where $M = mn$ is the amount of water in grams, and R_0 the specific gas constant. Since for highly diluted solutions $de = 0$, the ratio of the pressure $P : P_0$ is independent of the temperature.

This formula was proven by Kirchhoff * in 1858, from the observations of Regnault on the vapor tensions of different mixtures of sulphuric acid and water, and from those of J. Thomsen on the heat of evaporation of the same mixtures, and the results were found to correspond very well with those obtained practically. The student is referred for further information on this subject to Zeuner's Tech. Thermodynamics, II, p. 38.

* Pogg. Ann. 103.

CHAPTER VI.

THE RELATION BETWEEN HEAT AND ELECTRICAL ENERGY.

THE equation $dE = dQ + dA$, which expresses the change in the intrinsic energy E that takes place by the absorption of heat dQ and volume energy dA, hold also, according to our principle of energy, when dA represents any other form of energy. Further, all the consequences which have been developed in the previous chapters hold, when this other form of energy is treated in a corresponding way to that of $-pdV$, the volume energy. The way of considering natural processes, which is known as energetics, brings into the foreground of interest the similarity of the different forms of energy, and allows us to carry over the conclusions obtained for one special part, to other parts.

Corresponding to the way in which volume energy was treated, we can now treat the electrical energy of a current.

First, we must recall Ohm's law. If a current of electricity of the strength of J amperes* flows through

* According to the international agreement, we have the following definitions for the practical units:

1 *Ohm* is equal to the electrical resistance of a column of mercury

a conductor, with an electromotive force equal to Δ volts; and this conductor passes between two surfaces of constant potential (P_1 and P_2 volts), then

$$JW = P_1 - P_2 + \Delta, \tag{1}$$

where W is the constant of the conductor, lying between the two potential surfaces, which is called the resistance, and whose unit is 1 ohm. We will assume that the current goes from P_1 to P_2, i.e., $P_1 > P_2$. If we apply this equation for all parts of a simple circuit and add them together, we obtain, since the final potential of each part is equal to the initial potential of the following one, the relation

$$J \cdot \Sigma W = \Sigma \Delta, \tag{1b}$$

in which ΣW is the total resistance, and $\Sigma \Delta$ the total E. M. F. of the circuit.

The resistance of a prism of the length l cms. and the section of q cms.[3] is

$$w = \frac{1}{\sigma} \frac{l}{q},$$

where σ is the specific conductivity and $\frac{1}{\sigma}$ the specific resistance.

106.3 cms. long at the temperature 0° Cels., and whose mass is 14.452 grams, and whose section is uniformly equal. (∴ 1 sq. mm., since the sp. gr. of Hg is 13.5956.)

1 *Ampère* is the strength of a constant current that separates 0.001118 grams of silver in 1 second, by mean sun time, from a water solution of silver nitrate.

1 *Volt* is the potential difference at the ends of a conductor of 1 ohm resistance, through which a current of 1 ampère is flowing, and in which there is no E. M. F.

Further, from Joule's law the amount of energy delivered by the same conductor in one second is

(2) $$J^2W = J(P_1 - P_2 + \Delta) \text{ volt-amperes,}$$

which appears mostly in the form of heat; the conductor which takes the current J from potential P_2 to P_1 again would, were no E. M. F. present, give up, in the second, the amount of energy

(2*b*) $$J(P_2 - P_1) \text{ volt-amperes.}$$

In the whole circuit, therefore, the E. M. F. Δ causes the delivery of energy to the amount

(2*c*) $$J \cdot \Delta \text{ volt-amperes}$$

in 1 second, or in time dt the amount

(3) $$J \cdot \Delta \cdot dt \text{ volt} \times \text{amperes} \times \text{seconds.}$$

Since 1 volt $= 10^8$ absolute units of electrical potential, 1 ampere $= 1/10$ of an absolute unit of current strength; then (page 21)

$$1 \text{ volt} \times \text{ampere} \times \text{second} = 10^7 \text{ erg} = \frac{1}{4.24} \text{ cals.}$$
$$= 0.24 \text{ cals.;}$$
$$1 \text{ volt} \times \text{ampere} = 1 \text{ watt} = 0.24 \frac{\text{cals.}}{\text{sec.}}.$$

Finally, if we designate the product Jdt as the amount of electricity in the conductor during time dt, so that according to the usual way of consideration, one half of this amount, as positive electricity, goes

through the conductor in one direction, and the other half, as negative electricity, goes in the opposite one, and place

$$Jdt = d\epsilon, \tag{4}$$

we obtain for the equation of energy, for the portion of the conductor considered,

$$dE \leqq \theta dS - \Delta . d\epsilon. \tag{5}$$

Here E is the intrinsic energy, θ the absolute temperature, and S the entropy of that portion of the conductor that lies between the potential surfaces. $\Delta d\epsilon$ is, as already remarked, the total energy which comes from the E. M. F. for that portion of the conductor, and can therefore also appear partly as Joule's heat, developed in the conductor. Finally, θdS expresses the change of heat from other sources in the conductor.

Equation (5) stands now, in its form, and in the physical meaning of its quantities, in such complete analogy to (3) on page 80 that all the conclusions obtained there can be carried over to it. Of course Δ here is not, as p there, an intensity quantity (page 43), but is the difference between two such quantities, i.e., the potentials. If now, in general, we designate the potential by P, the second member of the equation falls into two members of the form $Pd\epsilon$ that stand in energetical analogy to $-pdV$ (*IdM* on page 43); in fact, an electrical current is only possible between two places of different potential, and the total amount of electricity is an unvarying quantity. Here we can

liken, as is usual, the electrical energy to a water-pipe connected with a pump, i.e., represent electrical energy as volume energy.

The method of reaching conclusions that was used on page 80 leads now from equation (5) to the law

$$\Delta Q = \theta \cdot \frac{\partial \Delta}{\partial \theta} \cdot \Delta\epsilon. \tag{6}$$

If we change the E. M. F. reversibly with the temperature, then for the discharge of electricity equal to $\Delta\epsilon$ through a conductor, in which the E. M. F. as well as the temperature θ is kept unchanged, we need a supply of heat equal to ΔQ, which is proportional to θ and to $\Delta\epsilon$, besides being proportional to the fall of potential.

According as Δ is an increasing or a decreasing function of θ, heat must be supplied or withdrawn, in order that the E. M. F. does work, without change of temperature; that is,

$$\Delta E = \theta^2 \frac{\partial}{\partial \theta}\left(\frac{\Delta}{\theta}\right) \cdot \Delta\epsilon. \tag{7}$$

This law (6), discovered by v. Helmholtz, holds for all reversible transformations of heat into current energy, for example, also for thermo-elements; but here we will follow out only the case for galvanic batteries.

In these the energy caused by the E. M. F. is occasioned by chemical changes that take place in the cell. According to Faraday's electrolytic law, there wanders from the anode to the kathode, with the

amount of electricity 1 ampere × second = 1 coulomb, a determined amount of hydrogen, namely,

$$\frac{1}{e_0} = x_0 = 0.00001036 \text{ grams},$$

whenever H is electrolytically separated. In general, there will be separated of the chemical elements present an amount equal to

$$\frac{\alpha}{e_0} = x_0\alpha = 0.00001036 . \alpha \text{ grams}.$$

where α is the chemical equivalent weight of the element considered. x_0 is found to be, from the electrolytic separation of silver, 0.001118 : 107.938. The equivalent weights are found from the atomic or molecular weights by division by small whole numbers, the valences; for example,

for	H	Cl	O	N
equivalent =	1	35.5	$8 = \frac{16}{2}$	$4.67 = \frac{14}{3}$.

Some elements, as mercury, have different equivalents in different compounds; for example, for Hg in $HgCl_2$ we have $\frac{199.8}{2}$, while in HgCl we have 199.8. Since, however, by the same current,

$$H - Cl, \ \frac{1}{2}\left(\begin{matrix} H \\ H \end{matrix} > O\right), \ \frac{1}{3}\left(\begin{matrix} H \\ H \\ H \end{matrix} > N\right),$$

$$\frac{1}{2}\left(Hg < \begin{matrix} Cl \\ Cl \end{matrix}\right), \ \frac{1}{2}\left(\begin{matrix} HgCl \\ HgCl \end{matrix}\right) = HgCl$$

are decomposed, we can say that for equal currents, in the same time, the same number of valences are dissolved.

With 1 equivalent there wanders always $e_0 = \frac{1}{x_0}$ = 96,540 coulombs.

When the chemical process which takes place in the cell is so carried out that it can cause no current, as in a calorimetric bomb, then the change of intrinsic energy, which takes place in the bomb, is shown wholly as heat. We will assume that by the decomposition of the number of grams of the electrolyte, as is expressed by the equivalent weight, the decrease of the intrinsic energy ΔE is measured by q cals. Then by the discharge of 1 coulomb the intrinsic energy of the cell sinks by xq cals., and equation (7) gives

$$-xq \text{ cals.} = \left(\frac{\partial \Delta}{\partial \theta} - \Delta\right) \text{ volt-amperes-seconds}$$

$$-4.24 \times 0.00001036q = \theta\frac{\partial \Delta}{\partial \theta} - \Delta \text{ cals;}$$

$$0.00004393q = \Delta - \theta\frac{\partial \Delta}{\partial \theta}$$

$$(8) \quad q = 228_{00}\left(\Delta - \theta\frac{\partial \Delta}{\partial \theta}\right) \text{ cals.} = 23\left(\Delta - \theta\frac{\partial \Delta}{\partial \theta}\right) \text{ Cals.}$$

The older theory of the galvanic element left out this second member of the right-hand side; as observed, this was rectified by v. Helmholtz.* The heat of reac-

*v. Helmholtz, Zur Thermodynamik chemischer Vorgänge 1882, 1883, in Ges. Abhandl. Gibbs recognized before that (1878) the connection between heat and current energy.

tion, produced by the decomposition of a chemical equivalent weight, is therefore greater or smaller than the E. M. F., expressed as heat, according as this is an increasing or a decreasing function of the temperature.

For the proof and use of the theory the following examples will suffice. They are taken principally from the observations of Jahn.*

The E. M. F. of a Daniell cell is $\Delta = 1.0962$ volts, corresponding to $1.0962 \times 23 = 25.2$ Cals. On the other hand, it is observed that, by the transformation of 1 mol or 2 equivalents, the intrinsic energy of the cell is decreased by 50.1 Cals., therefore by transformation of 1 equivalent by 25.05 Cals. By the formation of a half mol of $ZnSO_4$ from Zn, O, and highly diluted H_2SO_4 there are 53045 Cals. developed, and by the formation of a half mol of $CuSO_4$, correspondingly, 27980 Cals. The difference is 25.065 Cals. The small difference between this calorimetrical and the electrical determination leads us to suspect that the E. M. F. is almost entirely independent of the temperature. In fact Gockel observed $\frac{\partial \Delta}{\partial \theta} = 0.000034$ volts, which corresponds to $23 \times 273 \times 0.000034 = 0.21$ Cals.

A greater influence of the temperature coefficient is shown in the following cases:

An element consisting of lead and copper, which are suspended in their acetates, and separated from each other by a clay cell, gave the E. M. F. 0.47643 volts = to 10.96 Cals. for 1 equivalent, or 21.9 Cals. for

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* Wied. Ann. 28.

1 mol. Since we observe calorimetrically only 16.5 Cals., the remaining 5.4 Cals. must be taken from the surrounding objects. From the observation, $\frac{\partial \Delta}{\partial \theta} =$ 0.000385 volts, it follows $23 \times 273 \times 0.000385.2 = 4.8$ Cals., which is taken up as above mentioned.

If, on the other hand, silver and lead are present in their nitrates, the E. M. F. 0.932 volts leads to 42.9 Cals., while, calorimetrically measured, we find 50.9 for the transformation of 1 mol. Here q is greater than 23Δ, i.e., during an isothermal action the cell will give off heat to surrounding objects, or when this is not possible to give it off, it will be absorbed by the cell, and this is consequently heated. The absorption of heat amounts here to -8 Cals., while from $\frac{\partial \Delta}{\partial \theta} =$ 0.00063235, -7.9 follows

From the results of the "physikalisch-technischen Reichsanstalt," the E. M. F. of a Clark* cell, between 10° and 30° Cels., is

$$\Delta = 1.438 - 0.00116(\vartheta - 15) - 0.00001(\vartheta - 15)^2$$

How many per cent of its E. M. F. causes the absorption of heat? From (6) it follows that the heat absorbed by passage of 1 coulomb is

$$\Delta Q = \theta \frac{\partial \Delta}{\partial \theta};$$

---

*The Clark cell consists of Hg and Zn separated by a paste of $HgSO_4$, the Zn being in a saturated solution of zinc sulphate, and the whole made air-tight with paraffine.

therefore its ratio to the E. M. F. at 15 Cels. is

$$\frac{\Delta Q}{Q} = \frac{\theta \partial \Delta}{\Delta \partial \theta} = \frac{288}{1.438}(-0.00116) = -0.23;$$

i.e., 23% of the E. M. F. is given up to surrounding objects. The chemical process gives 123%.

An important law, concerning the process in a galvanic battery, can still be derived, from this manner of development, when we apply the principle of the conservation to a portion of the electrolyte lying between two potential surfaces. In this case, besides the changes of heat and current energy, considered in (5), we must also bring in the changes of substances, as possible changes, as was done on page 75.

We will restrict ourselves to the case of reversible changes and stationary state of the current. Let on the entrance-surface of the current the amount of matter dM, whose chemical intensity is Π_1 (unvariable), be taken up; on the other side let the same dM, with the chemical intensity Π_2, be carried farther. If, further, between the two potential surfaces the E. M. F. Δ is active, then the amount of energy used up by the transmission of the amount of electricity $d\epsilon$ is $\Delta d\epsilon$. Finally, it follows, from the condition that the state is now stationary, that no change of entropy or energy takes place, so that

$$(9) \qquad dE = 0 = -\Delta d\epsilon + \Pi_1 dM - \Pi_2 dM.$$

Electrical exchanges have, however, the property in electrolytes, that with a certain amount of elec-

tricity goes a certain amount of matter; namely, according to page 70,

$$dM = x_0 \alpha \,.\, d\epsilon. \tag{10}$$

Therefore it follows that

$$dE = 0 = [(\Pi_1 - \Pi_2) x_0 \alpha - \Delta] d\epsilon, \tag{9b}$$

an equation that can hold only when the transmission is reversible and stationary, when

$$\Delta = x_0 \alpha (\Pi_1 - \Pi_2). \tag{11}$$

The difference of the electrical potential, caused by the reversible stationary chemical process which is present in the two surfaces of constant potential, is proportional to the difference of chemical intensities, measured in equivalents of these surfaces. Since now every chemical reaction is occasioned by intensity differences, then, as will be shown later, every electrometer is a chemometer. (Ostwald.)

At any rate, by the foregoing considerations we can perceive the true nature of the E. M. F. from chemical sources; it appears to be equivalent to the loss of chemical intensity, as the energy of the electrical current is equivalent to the chemical energy.

According to equation (11), with the aid of (1), we can place

$$x_0 \Pi \alpha = P \epsilon_0 = \Pi \alpha; \tag{11b}$$

i.e., Π suffers a strain when P does, and therefore so does every seat of the E. M. F. If by dE we understand the amount of energy which goes through a certain

section, and under dS, dM, and $d\epsilon$ the amounts of entropy, matter, and electricity which wander with it, then

$$dE = \theta dS - Pd\epsilon + \Pi dM. \tag{12}$$

It remains now only to bring the conception of *conductivity* more exactly into view, and to join it to the ideas of the transportation of electricity and of matter, which takes place during electrolysis.

The strength of the current that flows in direction x through a prism of the length dx, with the specific conductivity σ and the section q, is equal to, according to Ohm's law, when for the length dx the potential increases by dP,

$$J = -\sigma \frac{dP}{dx} q. \tag{13}$$

The amount of electricity which goes through the section in a second is

$$i = -\frac{dP}{dx} \tag{13b}$$

With this amount of electricity $x_0\alpha_1 i$ grams of the anion goes to the kathode, and $x_0\alpha_2 i$ grams of the kation goes to the anode, and $x_0\alpha i$ grams of the electrolyte is decomposed in the second.

If the anion wanders with the velocity u_1 and the kation with the velocity u_2, and if $N\eta$, of the N equivalents present in a cubic centimeter, are electrolysed, or separated in their ions (i.e., if there are $N\eta$ equivalents of each ion in 1 cc.), then $N\eta u_1$ anion equivalents and $N\eta u_2$ kation equivalents wander in the second, on

which there is bound $N\eta u_1/x_0$ and $N\eta u_2/x_0$ coulombs of electricity respectively.

If now we accept the hypothesis of F. Kohlrausch* that these currents are independent of one another and each moves under the influence of the above potential difference, then

$$(14) \qquad \frac{N\eta u_1}{x_0} = -\sigma_1 \frac{\partial P}{\partial x}, \quad \frac{N\eta u_2}{x_0} = -\sigma_2 \frac{\partial P}{\partial x},$$

where the *hypothetical* specific conductivities σ_1 and σ_2 are to be so chosen that

$$(14b) \qquad \sigma_1 + \sigma_2 = \sigma;$$

while

$$(15) \qquad \frac{N\eta(u_1 + u_2)}{x_0} = i$$

is the total amount of electricity in motion. If we call the conductivity of each equivalent present μ, so that

$$(16) \qquad \mu N = \sigma,$$

where now μ is the *molecular conductivity*, and transform the hypothetical conductivities of the ions in a corresponding way,

$$\eta\mu_1 N = \sigma_1, \quad \eta\mu_2 N = \sigma_2, \quad \eta(\mu_1 + \mu_2) = \mu,$$

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* Wied. Ann. 6, 1876.

then

$$(18)\qquad \left\{\begin{array}{c} \dfrac{\eta}{x_0}u_1 = -\eta\mu_1\dfrac{\partial P}{\partial x}, \quad \dfrac{\eta}{x_0}u_2 = -\eta\mu_2\dfrac{\partial P}{\partial x}, \\ \dfrac{i}{N} = \dfrac{\eta}{x_0}(u_1+u_2) = -\mu\dfrac{\partial P}{\partial x}, \end{array}\right\}$$

$$(19)\qquad \frac{u_1}{u_2} = \frac{\mu_1}{\mu_2}.$$

The hypothetical molecular conductivities of the ions are therefore proportional to their wandering velocities. From (17) and (19) it follows that

$$(20)\qquad \eta\mu_1 = \mu\frac{u_1}{u_1+u_2}, \quad \eta\mu_2 = \frac{u_2}{u_1+u_2};$$

therefore by total dissociation into ions, i.e., for $\eta = 1$, where μ_∞ is the value of the molecular conductivity, we have

$$(20b)\quad \mu_1 = \mu_\infty \cdot \frac{u_1}{u_1+u_2}, \quad \mu_2 = \mu_\infty \cdot \frac{u_2}{u_1+u_2}, \quad \mu_1+\mu_2 = \mu_\infty.$$

F. Kohlrausch gives as molecular conductivity μ^*; the specific conductivity of a substance, with mercury as a standard, divided by the number of gram equivalents in a liter. That is,

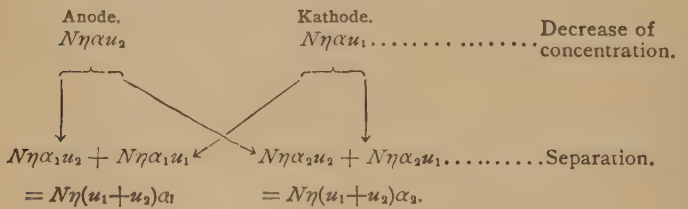
$$\mu^* = \frac{\sigma}{\sigma_{Hg}} : 1000N,$$

where σ_{Hg} is the specific conductivity of mercury. By the aid of (17) we then have

$$\mu_1 = \mu_1^* . \sigma_{Hg} \frac{1000}{\eta}, \quad \mu_2 = \mu_2^* . \sigma_{Hg} . \frac{1000}{\eta}, \quad \mu^* = \mu_1^* + \mu_2^* .$$

The specific conductivity may be found from the definition of the ohm. It is, in absolute units, $\sigma_{Hg} = 1.063 . 10^{-6}$.

The ratio of the *wandering velocities* can now be obtained, according to Hittorf, from the changes in concentration of the electrolyte at the electrodes. The wandering of $N\eta u_1$ equivalents of the anion means that at the kathode, in the second, each cubic centimeter loses the amount of $N\eta u_1$ equivalents of the electrolyte, these equivalents being separated out. If α is the equivalent weight of the electrolyte, α_1 that of the anion, and α_2 that of the kation, then the following scheme gives the number of grams in the second that wander or are separated :



The total amount separated is $N\eta\alpha(u_2 + u_2)$, which stands in the following proportions to the decrease of concentration which accompanies it :

$$(21) \quad Z_2 = \frac{N\eta\alpha u_2}{N\eta(u_1+u_2)\alpha} = \frac{u_2}{u_1+u_2}, \quad Z_1 = \frac{u_1}{u_1+u_2}, \quad \frac{Z_1}{Z_2} = \frac{u_1}{u_2}.$$

For example, Hittorf passed a current of 0.0626 amperes, for four hours, through a copper-sulphate solution which contained 2.8543 grams of CuO, as determined for a certain volume by KOH. After the current had passed through, the same volume of solution, taken from the neighborhood of the kathode, gave only 2.5897 grams of CuO, and the loss of copper, corresponding to 0.2646 grams CuO, is 0.2112 gram. This number, by a simple calculation, will give the value of $u_1\alpha_2$. During the passage of the current 0.2955 gram is separated as kation, from which, by the same calculation, we can find $(u_1 + u_2)\alpha_2$. From the anode the amount $0.2955 - 0.2112 = 0.0843$ gram Cu is carried over. The quotient,

$$Z_2 = \frac{u_2}{u_1 + u_2} = \frac{0.0843}{0.2955} = 0.285,$$

is called by Hittorf the transference number (Ueberführungszahl) of the kation. The value following from this,

$$Z_1 = \frac{u_1}{u_1 + u_2} = 1 - 0.285 = 0.715,$$

is the transference number of the anion, and gives the amount of the anion $u_1\alpha_1$ which has wandered, since during the time of observation, in each second, $u_1 + u_2$ equivalents, or $(u_1 + u_2)\alpha_1$ grams, of the anion SO_4 must be separated.

In another experiment a current of 0.1428 ampere was employed for two hours, and 0.3372 gram of Cu

were separated on the kathode. The solution around the kathode gave before the experiment 2.8543 grams and afterward 2.5541 grams of CuO, so that there was a loss of 0.3002 gram of CuO, corresponding to 0.2396 gram of Cu. The amount transferred is therefore 0.0976 grams Cu, and the transference number of the kation is $\frac{0.0976}{0.3372} = 0.289$, and that of the anion 0.711—which corresponds with the other experiment.

For highly diluted solutions Hittorf found the transference number for Na = 0.380, and Kohlrausch found the limit (grenzwerth) of the conductivity (18°)

$$\mu^* = 102.8 \times 10^{-7}.$$

From the relations

$$\frac{\mu_2^*}{\mu_1^* + \mu_2^*} = 0.380, \quad \mu_1^* + \mu_2^* = 102.8,$$

the hypothetical conductivities are found to be

$$\mu_1^* = 63.7 \,.\, 10^{-7}, \quad \mu_2^* = 39.1 \,.\, 10^{-7},$$

which are proportional (19) to the wandering velocities.

For KCl in the same way

$$\frac{\mu_2^*}{\mu_1^* + \mu_2^*} = 0.491, \quad \mu_1^* + \mu_2^* = 121.6 \,.\, 10^{-7};$$

therefore,

$$\mu_1 = 61.9 \,.\, 10^{-7}, \quad \mu_2^* = 39.7 \,.\, 10^{-7}.$$

The chlorine has in both cases approximately the same value, an average of 62.8, which is also supported

by other electrolytes. The still present uncertainties in the conductivities are decreasing by continued careful work.

The conductivity of silver has been very carefully determined by Loeb and Nernst for numerous cases and found in average to be 59.1. $AgNO_3$ gave 59.2, $AgClO_3$ 58.5 at 25° Cels. The latest collections of the conductivities can be found in Wied. Ann. 50. (Kohlrausch.)*

* See also Ostwald's Lehrbuch der allg. Chem. II.—TRANS.

PART III.

THE CHEMICAL INTENSITY.

CHAPTER I.

THE GENERAL PROPERTIES OF CHEMICAL INTENSITY.

It is now time to show how we are to treat changes of energy that are caused by an exchange of substance.

If the energy of a body changes, not only by absorption or loss of heat and volume energy, but also by gain or loss of mass, then the differential of the energy is given by the formula

$$(1)\quad dE \leqq \theta dS - pdV + \Pi_1 dM_1 + \Pi_2 dM_2 + \ldots + \Pi_n dM_n.$$

Here E, S, and V are respectively the intrinsic energy, entropy, and volume of the body, θ its temperature (absolute), and p the pressure under which it is. Further, $M_1, M_2, \ldots M_n$ are the masses of the chemical constituents of the bodies which are in the state of exchange, and $\Pi_1, \Pi_2, \ldots \Pi_n$ their chemical intensities.

That the function Π—which expresses mathematically the differential quotient of the function E with respect to M—possesses the physical properties to entitle it to the name of an intensity quantity, was shown for a simple case on page 78. The general proof follows below. It is not possible now, as then, to consider only two phases, for, in general, it is not possible to realize this without having at the same time exchanges with other phases.

We imagine a system of m phases, i.e., bodies that are in a state of exchange, and let each phase contain all or some of the n substances whose total masses, in the whole system, are given by $M_1, M_2, \ldots M_n$.

The changes of these substances we will assume to be *independent* of each other, i.e., an increase or decrease of one is possible without a change in the amounts of the others. Each phase is therefore a mixture and not a chemical compound of these n substances. If we distinguish now the values of the functions which belong to each phase in equation (1) by accents (as $'$, $''$, $'''$, etc.), then the energy equations for the single phases are

$$(2)\quad \begin{cases} dE' \leqq \theta' dS - p' dV' + \Pi_1' dM_1' \\ \qquad\qquad + \Pi_2' dM_2' + \ldots \Pi_n' dM_n', \\ dE'' \leqq \theta'' dS'' - p'' dV'' + \Pi_1'' dM'' \\ \qquad\qquad + \Pi_2'' dM_2'' + \ldots \Pi_n'' dM_n''. \end{cases}$$

And there are as many equations as there are phases, m, present. The m phases are, however, to be so chosen that no exchange of matter takes place except

between them, and that changes of heat and volume take place only inside the system, as it does in case of equilibrium. The system is therefore *isolated*, and no changes of energy are possible but the internal ones which occur between the phases. Then

$$dE = dE' + dE'' + \ldots = 0. \tag{3}$$

$$\begin{cases} dS' + dS'' + \ldots = 0\dagger, \\ dV = dV' + dV'' + \ldots = 0. \end{cases} \tag{4}$$

$$\begin{cases} dM_1 = dM_1' + dM_2'' + \ldots = 0, \\ dM_2 = dM_2' + dM_2'' + \ldots = 0. \end{cases} \tag{5}$$

These equations are to be considered as limits to the otherwise arbitrary differentials which occur in (2); and we will now treat the case further under the condition that no other limits exist but these, which follow from the conception of an isolated system.

If we add the equations in (2), it follows from (3) that

$$\begin{cases} 0 \leqq \theta' dS' + 0'' dS'' + \ldots + \Pi_1' dM_1' + \Pi_1'' dM_1'' + \ldots \\ -p' dV' - p'' dV'' - \ldots + \Pi_2' dM_1' + \Pi_2'' dM_2'' + \ldots \\ \qquad\qquad + \ldots \end{cases} \tag{6}$$

Now we can express each of the quantities in equations (4) and (5) by the $m - 1$ others; for example,

$$dV' = -dV'' - dV''' - \ldots$$

Accordingly we can re-form (6) into

$$-(p' dV' + d'' dV'' + \ldots) = -[(p'' - p')dV'' + (p''' - p')dV''' + \ldots$$

† This sum does not, in all cases, equal the entropy of the system (see page 70).

When, in this manner, we transform all the constituents of equation (6), then the differentials are completely independent of one another, provided that there are no other conditions than those expressed by equations (4) and (5). We can therefore, for example, place all the differentials up to dV'' equal to zero; we then find, since dV'' can assume any positive or negative infinitely small value, that it is necessary for the truth of equation (6) that $p'' - p' = 0$. From this well-known method of conclusion it follows that

$$\begin{cases} \theta' = \theta'' = \theta''' = \ldots = \theta, \\ p' = p'' = p''' = \ldots = p. \end{cases} \tag{7}$$

$$\begin{cases} \Pi_1' = \Pi_1'' = \Pi_1''' = \ldots = \Pi_1, \\ \Pi_2' = \Pi_2'' = \Pi_2''' = \ldots = \Pi_2. \end{cases} \tag{8}$$

When the temperatures and pressures of all the phases of an isolated system are equal, then the chemical intensities of all the constituents are equal also, when there is no other condition to the exchange of matter than the law of the conservation of matter.

This law has only one exception, i.e., in cases where it is not possible for a positive and a negative change of the differential to take place. The volume and entropy of a phase, as well as the masses of its single constituents, can, under all circumstances, increase or decrease, and we will assume here that new phases appear in the process; or that during it new constituents enter into them which were previously not there. The first case, that of the formation of a new phase, cannot be reconciled to the conditions that are expressed for the differentials by (3), (4), and (5), and

must therefore be excluded. On the other hand, new constituents can enter into a phase during the process, as, for example, in phase M_1, by which its differential, in the example dM_1', can assume only positive values. Since by this the other differentials in equation (6) can be placed equal to zero up to dM_1'' (or dM_1''', etc.), which, according to (5), must be chosen as negative, we have

$$\Pi_1' dM_1' + \Pi_1'' dM_1'' + \ldots$$
$$= (\Pi_1'' - \Pi_1') dM_1'' + (\Pi_1''' - \Pi_1') dM_1''' + \ldots ;$$

i.e., the intensities of the constituents in the phases which are newly added can not be *smaller* than the others. In the example

$$(7b) \qquad \Pi_1' \geqq \Pi_1'', \quad \Pi_1' \geqq \Pi_1''', \text{ etc.}$$

It is necessary to add to this proof, originated by W. Gibbs,† still the following:

Equation (2) gives, with help of (3), (4), and (5),

$$dE \leqq 0.$$

And in the case that relation (7*b*) is true, this inequality is the more fulfilled.

It agrees with (1), in case $dS = dS' + \ldots$, only when the equality sign is true in (1), i.e., when the process is reversible. Only reversible processes allow, therefore, the assumption of the conservation of entropy in an isolated system; if in such a system non-reversible processes take place, then it is not possible to exclude

† W. Gibbs, Thermodynamische Studien, German by Ostwald, Leipzig, 1892; or Trans. of the Conn. Academy, vols. II and III, 1873–78.

the case in which the entropy of the system varies from the sum of the entropies of the parts.

The functions can be found in the case of a gas mixture, since for this the energy, entropy, and volume are known as functions of the pressure and temperature. If we apply equation (1) to a gas mixture, we understand by dE the change that the intrinsic energy suffers when changes of heat, volume, and amounts, of the single gaseous constituents, are possible. We write (1) in the form

$$(8)\quad dE - \theta dS + PdV \leqq \Pi_1 dM_1 + \Pi_2 dM_2 \ldots + \Pi_n dM_n,$$

in which we represent by P the total pressure (page 68) of the gas mixture to distinguish it from the partial pressures $p_1, p_2, \ldots p_n$ of the single constituents.

By equation (13) (page 52) the energy for the unit of weight of a gas, whose specific heat by constant volume is c_v, at the absolute temperature θ, equals

$$(9)\quad e = e_0 + c_v\theta$$

when e_0 is a constant. The amount M grams of this gas possesses, then, the energy

$$Me = Me_0 + Mc_v\theta,$$

whose differential is

$$edM + Mc_v d\theta.$$

If we apply this to all the single different constituents of the mixture, distinguished by indices, the energy differential of the mixture follows, as

$$(10)\quad dE = (e_1 dM_1 + e_2 dM_2 + \ldots) + (M_1 c_{v_1} + M_2 c_{v_2} + \ldots)d\theta.$$

On the other hand, equation (14) (page 70) gives the entropy of the unit of weight of a gas whose volume is V, and whose gas constant is R, as

$$s = s_0 + R l V + c_v l \theta R - R l M. \tag{11}$$

The amount of M grams of this gas has then the entropy Ms, the differential of which is

$$MR\frac{dV}{V} + Mc_v\frac{d\theta}{\theta} - RdM + sdM.$$

Under the condition that the mixture of the single gases is a reversible process, the addition of the single entropies gives the total entropy. The total entropy of the whole system changes, therefore, by the amount

$$\begin{aligned} dS = {} & (M_1R_1 + M_2R_2 + \ldots)\frac{dV}{V} \\ & + (M_1c_{v_1} + M_2c_{v_2} + \ldots)\frac{d\theta}{\theta} \\ & - (R_1dM_1 + R_2dM_2 + \ldots) \\ & + (s_1dM_1 + s_2dM_2 + \ldots). \end{aligned} \tag{12}$$

If we transform this equation, remembering equation (7) (page 68), we obtain

$$PV = (M_1R_1 + M_2R_2 + \ldots)\theta, \tag{13}$$

and by substitution of these values (10) and (12) in (8) we find, since the expressions multiplied into dV and $d\theta$ cancel, and the left side of (8) contains only the differentials dM (as it must in consequence of the right side),

$$\begin{aligned} & (e_1 - \theta s_1 + R_1\theta\, dM + (e_2 - \theta s_2 + R_2\theta)dM_2 + \ldots \\ & \qquad \leqq \Pi_1 dM_1 + \Pi_2 dM_2 + \ldots \end{aligned} \tag{14}$$

If, now, the terms dM are entirely independent of one another, i.e., an actual gas mixture is considered, whose each constituent can increase or decrease entirely independent of the others, it follows from (14) that

$$(15)\quad \Pi_1 \geqq e_1 - \theta s_1 + \theta R_1, \quad \Pi_2 \geqq e_2 - \theta s + \theta R_2 \ldots$$

In consequence of the equation of state of a gas when the specific volumes are v_1, v_2, . . . , we have

$$(15b)\quad \Pi_1 \geqq e_1 - \theta s_1 + p_1 v_1, \quad \Pi_2 \geqq e_2 - \theta s_2 + p_2 v_2 \ldots;$$

i.e., the *chemical intensities* of each independent constituent of a gas mixture is, in reversible changes, *equal to the thermodynamical potential* of the unit of weight of this constituent, by constant pressure ; otherwise it is greater. From the consideration of equations (9) and (11), and the relation between the gas constant and the specific heats,

$$(16)\qquad c_p - c_v = R,$$

we find further that

$$(17)\quad \Pi_1 \geqq e_{01} + c_{p1}\theta - s_{01}\theta - \theta R_1 lV - c_{v1}\theta l\theta R_1 + \theta R_1 lM_1,$$

and the corresponding values for Π_2 and Π_3 . . . , which we will express in general (i.e., without indices), are given by

$$(17b)\quad \Pi \geqq e_0 + c_p\theta - s_{01}\theta - \theta RlV - c_v\theta l\theta R + \theta RlM.$$

If instead of equation (14), page 70 (above equation (11)), we use (13), on same page, for the transformation of (15), we obtain

$$(18) \quad \Pi \gtreqless e_0 + c_p\theta - s_0''\theta - c_p\theta l\theta + R\theta lP + R\theta lC,$$

$$(18b) \quad \Pi \gtreqless e_0 + c_p\theta - s_0\theta - c_p l\theta R + R\theta lP + R\theta lC,$$

where C is the concentration of the constituent to which the function Π belongs. Since $C = p/P$ (equation (9), page 69), it follows that

$$(19) \quad \Pi \gtreqless e_0 + c_p\theta - s_0\theta - c_p\theta l\theta R + R\theta lp.$$

By differentiation of (18) we find

$$\frac{\partial \Pi}{\partial C} \gtreqless \frac{R\theta}{C};$$

i.e., with increasing concentration of a gas in a mixture, when the temperature does not change, the intensity of the gas increases the slower, the greater the already present concentration is.

The law, proven on page 117, of the equality of the chemical intensities of the different phases of the same substance, allows us to draw into consideration the chemical intensities of other substances that are *not gaseous*. We will assume any solid or liquid body that contains one constituent that is independent, which is present in the concentration C. If, now, there is a gas mixture which contains the same independent

constituent in the same concentration C, at the same temperature and pressure, that is in contact with the solid or liquid, so that they form together an isolated system, then the constituent considered has the same intensity in the gas mixture and in the body. This intensity is

$$\Pi \geqq \Pi^* + R\theta lC, \tag{21}$$

where R is the specific gas constant for the constituent, and Π^* that function of θ and P which the intensity of the constituent would give were it alone, i.e., in concenntration 1.

According to (15b),

$$\Pi^* = e^* - \theta s^* + Pv^* \tag{22}$$

where e^*, s^* and v^* are the values of the energy, entropy, and volume of one gram of the gaseous constituent, which has the same chemical intensity as that in the body.

That such gas mixtures are to be found, at least in all cases of very small concentrations, is apparent. But also in cases with greater concentrations equation (21) has shown itself to be applicable in this way, that we assume in the substance other constituents than those which are generally considered as being present, For example, in a salt solution, water and NaCl, we assume also Na and Cl as constituents. This hypothesis, of Arrhenius, of the dissociation into ions has made it possible to apply formula (21) very widely, and to make it of great value.

In our subject, of the mathematical consideration of natural processes, the grounds for or against such an hypothesis need not be considered. We apply formula (21) to non-gaseous substances, and draw the mathematical consequences of the assumption.

The single condition that it is necessary to make in the property of the function Π, in order that our assumption may be upheld, is the following:

The energy equation (1) must remain true when by unchanged θ, P, $\Pi_1 \ldots \Pi_n$, all masses M_1, M_2, $\ldots$ M_n are proportionally increased. The value of each intensity must not change (but still it can be considered as a function of θ, P, M_1, M_2, $\ldots$ M_n) by a proportional increase of all the terms M. The expression C has, according to 9 (page 69), this property, therefore Π has it also.

The other properties which the function Π must show in the constituents of non-gaseous substances can be ascertained by the method which led to equation (2), page (80). We bring each of the equations (2),

$$dE \leqq \theta dS - PdV + \Pi_1 dM_1 + \Pi_2 dM_2 + \ldots + \Pi_n dM_n,$$

into the form

$$d(E - \theta S + PdV) \tag{23}$$

$$\leqq - Sd\theta + VdP + \Pi_1 dM_1 + \Pi_2 dM_2 + \ldots + \Pi_n dM_n.$$

Since the expression on the left is a complete dif-

ferential, it follows that, for all reversible processes, have we the equations

$$(24)\qquad \begin{cases} \dfrac{\partial \Pi_1}{\partial \theta} = -\dfrac{\partial S}{\partial M_1}, & \dfrac{\partial \Pi_1}{\partial P} = \dfrac{\partial V}{\partial M_1}, \\ \dfrac{\partial \Pi_1}{\partial M_2} = \dfrac{\partial \Pi_2}{\partial M_1}, \ldots & \dfrac{\partial \Pi_1}{\partial M_n} = \dfrac{\partial \Pi_n}{\partial M_1}. \\ \dfrac{\partial \Pi_2}{\partial \theta} = -\dfrac{\partial S}{\partial M_2}, & \dfrac{\partial \Pi_2}{\partial P} = \dfrac{\partial V}{\partial M_2}, \\ \dfrac{\partial \Pi_2}{\partial M_1} = \dfrac{\partial \Pi_1}{\partial M_2}, \ldots & \dfrac{\partial \Pi_2}{\partial M_n} = \dfrac{\partial \Pi_n}{\partial M_2}. \\ \ldots\ldots\ldots & \ldots\ldots\ldots \end{cases}$$

If we substitute the quantities v and s which are, in general, functions of the pressure, the temperatures, and the masses,

$$(25)\qquad \begin{cases} dV = v_1 dM_1 + v_2 dM_2 + \ldots + v_n dM_n, \\ dS = s_1 dM_1 + s_2 dM_2 + \ldots + s_n dM_n, \end{cases}$$

then

$$(26)\qquad \frac{\partial \Pi_i}{\partial \theta} = -s_i, \quad \frac{\partial \Pi_i}{\partial P} = v_i.$$

The equations which show the relations between the intensities and the masses, lead to a consequence which is worthy of notice. If Π_1 depends besides on P and θ, only on the concentration, then

$$(27)\qquad \begin{aligned} C_1 &= N_1 : (N_1 + N_2 + \ldots + N_n) \\ &= \frac{M_1}{m_1} : \left(\frac{M_1}{m_1} + \frac{M_2}{m_2} + \ldots \frac{M_n}{m_n}\right), \end{aligned}$$

and Π_2 in the same way depends on C_2, etc.

Here each N means the number of mols, m, of one of the n constituents, which are present in the phase considered. Now

$$\frac{\partial \Pi_1}{\partial M_1} = \frac{\partial \Pi_1}{\partial C_1} \cdot \frac{\partial C_1}{\partial M_2}$$

$$= -\frac{\partial \Pi_1}{\partial C_1} \cdot \left[\frac{M_1}{m_1} : \left(\frac{M_1}{m_1} + \frac{M_2}{m_2} + \cdots + \frac{M_n}{m_n}\right)^2\right] \frac{1}{m_2}$$

$$= -\frac{\partial \Pi_1}{\partial C_1} \cdot \frac{C_1}{m_2} : \left(\frac{M_1}{m_1} + \frac{M_2}{m_2} + \cdots \frac{M_n}{m_n}\right),$$

and the equations under (24) require that

$$(28a) \qquad -\frac{\partial \Pi_1}{\partial C_1} C_1 m_1 = \frac{\partial \Pi_2}{\partial C_2} C_2 m_2,$$

or, in general, that the expression

$$(28) \qquad \frac{\partial \Pi}{\partial C} \cdot C_1 m$$

has the same value for all constituents.

For gaseous constituents this value, by (20), is equal to $R_0\theta$; therefore we have, *for all constituents*,

$$\frac{\partial \Pi}{\partial C} = \frac{R_0\theta}{mC} = \frac{R\theta}{C},$$

or

$$\Pi = \Pi^* + R\theta lC,$$

which is the same as (21), where only one of the constituents is gaseous, to which the concentration C

refers; or where only one constituent is present which, by the same pressure and temperature in the gas mixture, can be in equilibrium with the substance.

The general utility of equation (21) is made dependent upon the assumption that the chemical intensity of each constituent of a body is a function only of its pressure, temperature, and concentration in the body. We have up to the present left an arbitrary choice of the independent constituents. Nothing prevents us from considering these (which have to fulfil no other condition than of being independent) as compounds themselves, and made up of other elementary constituents, as, e.g., of their ions. We will now *assume that it is possible so to define a constituent that the intensity of each one depends* (besides upon its temperature and pressure) *upon its concentration alone.* Then formula (21) holds. By the ionic hypothesis of Arrhenius, such a choice of the constituents, in solutions of electrolytes, is possible.

Just as we explain the apparent deviations from Avogadro's law by the proper assumption of the molecular decomposition into constituents, so in this case we succeed in bringing the facts under the general law by a proper choice of the chemical constituents of the phenomena. We look upon the hypothesis of Arrhenius, therefore, as a fitting definition of the conception of "chemical constituents."

To show the application of equation (21), we will give the E. M. F. which exists in two places in a liquid, which in consequence of different concentrations, C_1 and C_2, show a difference, $\Pi_1 - \Pi_2$, in their chemical intensi-

ties, but which are at the same temperature and pressure. From equation (11) (page 106) we obtain

$$\Delta = x_0 \alpha R \theta l \frac{C_1}{C_2}. \tag{29}$$

If the valence of the liquid is w, then the equivalent α equals $m:w$, where m is the molecular weight, and we have

$$\Delta = \frac{x_0}{w} R_0 \theta l \frac{C_1}{C_2}. \tag{29b}$$

The derivation by Gibbs of the *law of absorption* is another application of equation (21). If a gas stands over a liquid which absorbs it, then when equilibrium is reached the intensity of the pure gas is the same as that of the absorbed one, that is, when the pressure and temperature of the two phases have become equalized. If we designate by C_0 and C_0' the concentrations; by m_0 and m_0' the molecular weights, of the solvent in the liquid and gaseous phases; by C_1 and C_1' the concentrations; by m_1 and m_1' the molecular weights, of the gases in the solution, and in the vapor space over it; and if further A_0, A_0', A_1, and A_1' are functions of the pressure and temperature, then

$$A_0 + m_0 R_0 l C_0 = A_0' + m_0' R_0' l C_0',$$
$$A_1 + m_1 R_0 l C_0 = A_1' + m_1' R_0 l C_1'.$$

It follows, especially for the case that the vapor of the liquid possesses a negligible partial pressure as

against the gas in the vapor, i.e., the latter has the concentration $C_1' = 1$,

$$lC_1 = \frac{A_1' - A_1}{m_1 R_0},$$
$$C_1 = F(\theta, P).$$

That this function, F, of the pressure and temperature is for small absorption, i.e., small value for C_1, almost independent of the pressure, as Henry found, is established by (26) (page 125). For small C_1, A_1 is large in comparison to A_1', and A_1 varies, according to that formula, very slightly with the pressure.

CHAPTER II.

THE SIMPLE CHEMICAL REACTION.

WE turn again to equation (1) on page 114,

$$(1)\quad dE \leqq \theta dS - PdV + \Pi_1 dM_1 + \Pi_2 dM_2 + \ldots \Pi_n dM_n,$$

which holds for any substance that can take up or give out heat or volume energy, and which possesses n constituents, whose amounts can change independently of one another. We will now, however, consider a special kind of change between the constituents of the mixture, namely, *a chemical reaction*, whose special property is the existence of a stoichiometrical dependence between the n changes. By the decomposition of water, for example, we consider three independent constituents beside one another; they are water, oxygen, and hydrogen. These form, in each instant of the progress of the reaction, a mixture for which equation (1) holds; they *can*, by other influences, increase or decrease independently, but the chemical reaction restricts their freedom, in such a way that when we know the change of *one* of the three, which takes place during the process, we can also give the change of each of the other two.

We call the chemical reaction *simple* when, as in

this example, the changes of mass which take place at the same time are related so that from the change of *one* mass we can find the changes for the others. If the molecular weights of the substances, whose masses are $M_1, M_2, \ldots M_n$, are $m_1, m_2, \ldots m_n$, and if, in consequence of the stoichiometrical relations, $v_1, v_2, \ldots v_n$ mols of the substances enter with each other into chemical reactions, then we can place

$$(2) \quad dM_1 = v_1 m_1 dM_0, \quad dM_2 = v_2 m_2 dM_0, \ldots dM_n = v_n m_n dM_n.$$

The terms v we will call the "exchange numbers" (Umsatzzahlen) of the single substances in the reaction. dM_0 is a factor; if hydrogen takes part in the reaction with the "exchange number" 1, then dM_0 is the amount of H formed in an infinitely small element of time in the reaction. On the other hand we can imagine any one of the substances formed placed in a simple reaction with hydrogen with the "exchange number" 1. In the case of the decomposition of water, for example, we have, when we distinguish water, oxygen, and hydrogen by the indices 1, 2, and 3,

$$m_1 = 18, \quad m_2 = 32, \quad m_3 = 2.$$
$$v_1 = -2, \quad v_2 = +1, \quad v_3 = +2.$$

By this the stoichiometrical relation

$$H_2O = O + H_2, \quad \text{or} \quad 2H_2O = O_2 + 2H_2$$

is placed in (2) in the form

$$dM_1 = -2 \times 18 \,.\, dM_0, \quad dM_2 = 32 \,.\, dM_0, \quad dM_3 = 2 \times 2 \,.\, dM_0,$$

and the chemical meaning of dM_0 is made clear.

We will designate by M_0, the variable upon which alone the reaction depends, as the *parameter* of the reaction.

The addition of equations (2) gives, when the total mass is equal to M,

$$(2b) \qquad dM = (m_1 v_1 + m_2 v_2 + \ldots m_n v_n) dM_0,$$

where M can be placed instead of M_0.

By the substitution of the values in (2) in (1) we have

$$(3) \quad dE \geqq \theta dS - PdV + \{\Pi_1 v_1 m_1 + \Pi_2 v_2 m_2 + \ldots \Pi_n v_n m_n\} dM_0.$$

The factor of dM_0, which we will designate by Φ, can be calculated when all reacting constituents are perfect gases and form a homogeneous gas mixture. We obtain from equation (15), page 121,

$$(4) \quad \Phi \geqq (e_1 - \theta s_1 + R_1\theta) v_1 m_1 + (e_2 - \theta s_2 + R_2\theta) v_2 m_2 + \ldots;$$

and from equations (18) and (19), page 122,

$$(5) \quad \Phi \geqq E_0 + C_p\theta - S_0''\theta - C_p\theta l\theta + R_0\theta l P^{\nu} + R_0\theta l(C_1^{\nu_1} . C_2^{\nu_2} \ldots C_n^{\nu_n}).$$

$$(5b) \quad \Phi \geqq E_0 + C_p\theta - S_0''\theta - C_p\theta l\theta + R_0\theta l(p_1^{\nu_1} p_2^{\nu_2} \ldots p_n^{\nu_n}).$$

Here we use, according to (6), page 68,

$$R_0 = m_1 R_1 = m_2 R_2 = \ldots = 2 \text{ cals.}$$

and

$$(6)\quad \begin{cases} E_0 = e_{01}v_1 m_1 + e_{02}v_2 m_2 + \ldots, \\ S_0'' = s_{01}v_1 m_1 + s_{02}v_2 m_2 + \ldots, \\ \qquad\qquad + c_{p_1}v_1 m_1 lR_1 + c_{p_2}v_2 m_2 lR_2 + \ldots, \\ C_p = c_{p_1}v_1 m_1 + c_{p_2}v_2 m_2 + \ldots, \\ N = v_1 + v_2 + v_3 + \ldots \end{cases}$$

E_0 is therefore the energy and S_0'' the entropy of 1 mol of the reacting gas mixture for a certain standard state. C_p* is the molecular heat of the mixture for constant pressure, and N the sum of the "exchange numbers." Since the total change of mass is

$$(7)\qquad dM = (m_1 v_1 + m_2 v_2 + \ldots m_n v_n) dM_0,$$

then by (3)

$$(8)\qquad \frac{\Pi_1 m_1 v_1 + \Pi_2 m_2 v_2 + \ldots \Pi_n m_n v_n}{m_1 v_1 + m_2 v_2 + \ldots m_n v_n} = \Pi,$$

which we can designate as the chemical intensity of the reaction.

If the constituents are not perfect gases, but form a homogeneous mixture, then by (21), page 123,

$$(9)\qquad \Phi \gtrless \phi(\theta, P) + R_0 \theta l(C_1^{v_1} C_2^{v_2} \ldots C_n^{v_n}),$$

* The indices will distinguish these sufficiently from the concentrations.

where $\phi(\theta, P)$ is a function of the temperature and pressure, which is the value that the expression

$$(10) \qquad \Phi = \Pi_1 m_1 v_1 + \Pi_2 m_2 v_2 + \ldots \Pi_n m_n \nu_n$$

assumes, when each of the concentrations C_1, C_2, C_3, $\ldots C_n$ is equal to 1.

If the constituents do not form a homogeneous mixture, but belong to different phases, then we have to use the above equation for each phase and add them together.

We will now apply equation (3) to a case of chemical equilibrium. The reaction, we will assume, is finished, then changes of heat and volume energy do not take place, the energy does not change; but a continuance of the reaction either forward or backward is still possible, as, for example, a change in temperature or pressure would show.

In order that the left side of (3), dE, equals 0, since dM_0, dS, and dV have the same value, the factor of dM_0, i.e. Φ, must have the same sign as dM_0, as $dS = 0$ and $dV = 0$ show. If dM_0 can be chosen positive or negative, i.e., if the reaction is *reversible*, or if the chemical reaction can continue or go backwards, according to the same stoichiometrical laws, then

$$(10b) \qquad \Phi = \Pi_1 m_1 v + \Pi_2 m_2 v_2 + \ldots = 0.$$

or when A is a constant,

$$(11) \quad l(C_1^{\nu_1} C_2^{\nu_2} \ldots C_n^{\nu_n}) = -\frac{E_0}{R_0\theta} + \frac{C_p}{R_0} l\theta - lP^N + A,$$

$$(11b) \quad l(p_1^{\nu_1} p_2^{\nu_2} \ldots p_n^{\nu_n}) = -\frac{E_0}{R_0} + \frac{C_p}{R_0} l\theta + A,$$

in the case that all reacting gases are perfect; otherwise

$$(12) \qquad A(C_1^{\nu_1} C_2^{\nu_2} \dots C_n^{\nu_n}) = \psi(\theta, P),$$

a function of pressure and temperature of which we know nothing further.

Before we show the application of these important formulæ, we must observe that by the differentiation of (11

$$\frac{\partial}{\partial\theta} A(C_1^{\nu_1} C_2^{\nu_2} \dots C_n^{\nu}) = \frac{E_0}{R_0\theta^2} + \frac{C_p}{R_0\theta} = \frac{1}{R_0\theta^2}(E_0 + C_p\theta)$$

by constant pressure.

If we substitute $C_v + R_0 N$ for C_p, where C_v is the molecular heat of the mixture at constant volume, then by a simple operation we obtain

$$(13) \qquad \frac{\partial}{\partial\theta} A\left(\frac{C_1}{\theta}\right)^{\nu_1}\left(\frac{C_2}{\theta}\right)^{\nu_2} \dots \left(\frac{C_n}{\theta}\right)^{\nu_n} = \frac{1}{R_0\theta^2}(E_0 + C_v\theta).$$

A glance at formula (6) shows that $E_0 + C_v\theta$ is the intrinsic energy gained by the mixture, when the reaction has gone so far as to form 1 mol; therefore the negative heat of reaction for constant volume. Further, we see that $E_0 + C_p\theta$ is the intrinsic energy increased by the work of expansion, i.e., the negative heat of reaction for constant pressure. If by Q we designate the negative heat of reaction by constant pressure, then

$$(14) \qquad Q = + R_0\theta^2 \frac{\partial}{\partial\theta} A(C_1^{\nu_1} C_2^{\nu_2} \dots C_n^{\nu_n}).$$

It also follows from (11*b*) that

$$Q = + R_0\theta^2 \frac{\partial}{\partial\theta} l(p_1^{\nu_1} p_2^{\nu_2} \ldots p_n^{\nu_n}), \tag{14b}$$

and corresponding equations are obtained from (13) for the negative heat of reaction for constant volume. That equations (7) and (8), pages 81, 82, are special cases of these equations is apparent.

Equation (14) can be derived in another way, not only restricted to gases. We have

$$dS = \frac{\partial S}{\partial\theta} d\theta + \frac{\partial S}{\partial P} dP + \frac{\partial S}{\partial M} dM,$$

which for constant pressure and temperature goes over into

$$dS = \frac{\partial S}{\partial M} dM,$$

i.e., according to (24), page 125,

$$dS = -\frac{\partial \Pi}{\partial\theta} dM, \tag{15}$$

and the necessary supply of heat is

$$dQ = \theta dS = -\theta \frac{\partial \Pi}{\partial\theta} dM. \tag{15b}$$

If now the differential quotient $\frac{\partial \Pi}{\partial\theta}$ is independent

of the mass, then by integration, as on pages 81, 82, we have

$$(15c) \qquad \Delta Q = -\theta \frac{\partial \Pi}{\partial \theta} \Delta M.*$$

Between equations (8), (9), and (10), however, we have the relation

$$(16) \qquad \Pi = \Pi_0(\theta, P) + R\theta l(C_1^{\nu_1} C_2^{\nu_2} \dots C_n^{\nu_n});$$

and when, in consequence of the equation

$$R_1 m_1 = R_2 m_2 = \dots = R_0,$$

we place

$$(17) \qquad R_0 = R(m_1 \nu_1 + m_2 \nu_2 + \dots + m_n \nu_n),$$

and designate by Π_0 the value of Π for $C_1 = C_2 = \dots = 1$, and partially differentiate (16) with respect to θ, then

$$\frac{\partial \Pi}{\partial \theta} = \frac{\partial \Pi_0}{\partial \theta} + Rl(C_1^{\nu_1} C_2^{\nu_2} \dots C_n^{\nu_n}).$$

Since in case of equilibrium $\Pi = 0$, then

$$\Pi_0 = -R\theta l(C_1^{\nu_1} C_2^{\nu_2} \dots C_n^{\nu_n}).$$

It follows when the concentrations C are assumed as determining the equilibrium, therefore *dependent upon* θ, that

$$\frac{\partial \Pi}{\partial \theta} = -\theta R \frac{\partial}{\theta \partial} l(C_1^{\nu_1} C_2^{\nu_2} \dots C_n^{\nu_n});$$

---

* The Q used in this case is the *negative* heat, while on page 81 it is the *positive* heat, so that the two equations are precisely the same.—TRANS.

hence

$$\Delta Q = + R\theta^2 \frac{\partial}{\partial \theta} l(C_1^{\nu_1} C_2^{\nu} \ldots C_n^{\nu_n}) \Delta M. \tag{18}$$

The amount of heat which is to be supplied for the formation of 1 mol

$$\Delta M = m = m_1 \nu_1 + m_2 \nu_2 + \ldots m_n \nu_n$$

is therefore, in accordance with (17),

$$Q = + R_0 \theta^2 \frac{\partial}{\partial \theta} l(C_1^{\nu_1} C_2^{\nu_2} \ldots C_n^{\nu_n}), \tag{18b}$$

which is the same as (14), derived for gases alone.

This relation, as van't Hoff has already shown, means that *by increasing temperature each chemical reaction that absorbs heat goes forward, and each one that develops heat goes backward.*

The supply of heat at constant volume we find, according to a rule given in a previous chapter, from (13), as

$$Q' = R_0 \theta^2 \frac{\partial}{\partial \theta} l(C_1^{\nu_1} C_2^{\nu_2} \ldots C_n^{\nu_n}) - R_0 N' \theta, \tag{19}$$

where N' mols of gas are formed by the reaction.

By the integration of equations (18*b*) and (19) it is to be remembered that the heat of reaction depends upon the temperature of the same (see page 18).

Each of the two derivations of equation (13) can be used, when correspondingly altered, to develop the equation

$$V_0 = - R_0 \theta \frac{\partial}{\partial P} l(C_1^{\nu_1} C_2^{\nu_2} \ldots C_n^{\nu_n}), \tag{20}$$

in which $V_0 (= NR_0\theta/P)$ is the volume of as many mols in gaseous state, as the sum N of the "exchange numbers" is equal to. The formula follows in the same way as (14) by differentiation of (11), and also, in general, for non-gaseous bodies, by aid of (24) (page 125), namely,

$$\frac{\partial \Pi}{\partial P} = \frac{\partial V}{\partial M}.$$

There is one consequence of (14) that is worthy of notice. If a reversible reaction proceeds without development of heat, then we can only conclude that the product of the concentrations $C_1^{\nu_1} C_2^{\nu_2} \ldots C_n^{\nu_n}$, for the temperature of the reaction, is a maximum or a minimum, and the same holds true for (20). When, however, by the change of the temperature of reaction, there is no heat developed, then the concentration product is independent of the temperature. Also when by change of pressure no change of volume follows, then the concentration product is also independent of the pressure, i.e., in general, a constant. If this holds for greater concentrations, i.e., independent of the concentrations C, then it is only possible that these cancel one another, i.e., the concentration product is 1 and its logarithm is 0. In other words, then, no reaction takes place; the end product is the same as the initial; to each $C^{+\nu}$ there is a $C^{-\nu}$.

Since, by the phenomenon observed by Hess of the thermo-neutrality of dilute salt solutions, in many cases no heat is observed by mixing, we are led to the assumption that in these cases there is no reac-

tion, i.e., that such salt solutions are composed of substances that are not changed. These constituents we find to be the ions; the dissolved salts are dissociated into their ions, when we observe no heat development by the mixing of their solutions.

CHAPTER III.

CHEMICAL EQUILIBRIUM.

ACCORDING to equation (12) (page 135) a reversible chemical reaction can only come to rest, i.e., be in equilibrium, when the product of the concentrations and exchange numbers of the reacting constituents,

$$C_1^{\nu_1} C_2^{\nu_2} \ldots C_n^{\nu_n}, \tag{1}$$

possesses a certain value, which depends upon the temperature and pressure.

The concentration of a constituent, in a homogeneous mixture, is the ratio of the number N of its mols, to the total number, $N_1 + N_2 + \ldots + N_n$, in the phase (not in the system):

$$C = \frac{N}{N_1 + N_2 + \ldots + N_n},$$

according to (9) (page 69). Since now the sum of all the mols does not change, the product,

$$N_1^{\nu_1} N_2^{\nu_2} \ldots N_n^{\nu_n}, \tag{2}$$

is a quantity which is only dependent upon the temperature and pressure. The quantities N, which change

by continued reaction, are the amounts of the reacting constituents measured in mols. Each constituent is therefore to be measured by another unit, its mol.

If all reacting constituents in the system are gases, then we can assume (equation (11*b*), page 134) that the product,

$$p_1^{\nu_1} p_2^{\nu_2} \ldots p_n^{\nu_n}, \tag{3}$$

i.e., the partial pressures raised to the powers of the exchange numbers, must be independent of the pressures, and dependent only upon the temperature.

Since during a reaction the amounts of single constituents increase, and others decrease, the exchange numbers of some are positive and of others are negative. If now ν_a, ν_b . . . are the absolute values of the former, and ν_α, ν_β . . . the absolute values of the latter, then each of the characteristic products (2) and (3) can be written as the quotient of two such products; for example, the first assumes the form

$$\frac{N_a^{\nu_a} N_b^{\nu_b} \ldots}{N_\alpha^{\nu_\alpha} N_\beta^{\nu_\beta} \ldots} \tag{4}$$

In the numerator is the number of increasing mols, and in the denominator the number of decreasing ones.

This expression assumes a very convenient form when we measure the constituents in reaction equivalents νm, instead of mols; so that of all constituents, in the same time, an equal number of these units is transformed.

If at first we have A, B, . . . equivalents of the in-

creasing constituents, and $A, B, \ldots$ equivalents of the decreasing ones, then after the reaction we have $A + x$, $B + x, \ldots$ of the one, and $A - x, B - x, \ldots$ of the other, when x is the number of equivalents transformed.

If, for simplicity, we further designate the absolute values of the exchange numbers by $a, b, \ldots$ and $\alpha, \beta, \ldots$, then for the case of equilibrium we have

$$(5)\quad (A + x)^a (B + x)^b \ldots = K(A - x)^\alpha (B - x)^\beta \ldots,$$

where K is a function of pressure, and temperature. The determination of chemical equilibrium is therefore in all cases dependent only upon the solution of an algebraic equation. In this form the result of the last chapter was found by Guldberg and Waage in 1867, independently of the principles which we have used. Since then it has been proven for many important cases; we will now treat a few typical examples.

For the formation and decomposition of hydriodic acid according to the formula

$$H_2 + I_2 = 2HI,$$

when HI, H, and I are distinguished by the indices 1, 2, and 3, we must substitute in (3)

$$\nu_1 = 2, \quad \nu_2 = -1, \quad \nu_3 = -1.$$

We obtain

$$(6)\quad \frac{p_1^2}{p_2 p_3} = K,$$

where K is a function of the temperature independent of the pressure. If, at first, in one volume we have so much hydrogen and iodine, that their partial pressures are p_H and p_I, and the ratio of mixing is

$$z = p_I : p_H, \tag{7}$$

then after a very gradual reaction, when the reaction is at rest, a part of each of the substances has been used up for the formation of hydriodic acid, they are, from stoichiometrical grounds, equal to

$$p_H = p_2 + \frac{p_1}{2}, \quad p_I = p_3 + \frac{p_1}{2}. \tag{8}$$

If x is the ratio of the H still free, to that amount originally introduced, then

$$x = \frac{p_2}{p_H}; \tag{9}$$

and if, further, P is the total pressure of the mixture when in chemical equilibrium, then

$$P = p_1 + p_2 + p_3; \tag{10}$$

and it follows that

$$\begin{cases} p_1 = 2p_H(1 - x), & p_2 = p_H . x, \\ p_3 = p_I - p_H + p_H x, & P = p_H + p_I, \end{cases} \tag{11}$$

and equation (6) becomes

$$\frac{4(1 - x)^2}{x\left(\frac{p_I - p_H}{p_H} + x\right)} = K. \tag{12}$$

If at first equal amounts of H and I were introduced, or if at first only HI was introduced, then we can, according to Lemoine's experiments, take $x = 0.28$ approximately (Nernst). By this $K = 4 \cdot 0.72^2 : 0.28^2 = 26.45$, and by calculation we find $\frac{80}{3}$ or $26.0+$. If the state of equilibrium is observed for *one* mixture, then it is known for all. By aid of (7) we can write (12) in the form

$$4(1-x)^2 = Kx(z-1+x).$$

$$(13) \qquad (K-4)x^2 + Kxz - (K-8)x - 4 = 0.$$

By this for each z we can find the corresponding x, by solving an equation of the second degree, as Nernst has done. He finds, for example,

$z =$	1.000	0.784	0.527	0.258
$x =$	0.280	0.373	0.534	0.754

while Lemoine observed

$x =$ 0.240 to 0.290	0.350	0.547	0.774

It is simpler, however, to calculate the values of z for a few of x and then to interpolate the others. The graphic method, though little used in chemistry, is the one best adapted for a complete view of a process, and for the accuracy of observation. If x and z are considered as coordinates, then equation (13) gives a curve of the second order. If we transpose the x axis so that

$$z = z' + \frac{K-8}{K},$$

then the equation becomes

$$(14) \qquad (K-4)x^2 + Kxz' - 4 = 0,$$

which is a hyperbola, whose asymptotes are

$$x = 0, \quad \text{and} \quad \frac{z'}{x} = -\frac{K-4}{K},$$

which intersects the straight line $z' = 0$ in the two points, $x = \pm 2 : \sqrt{K-4}$. It goes also through the point $x = 1$, $z = 0$, and meets the x axis in the two points of intersection $x = (K - 8 \pm K) : 2(K-4)$, i.e., in the point $x = 1$ and in the point $x = -4 : (K-4)$.

Using as the value for K the one chosen by Nernst (as given above), we obtain the curve given in Fig. 6.

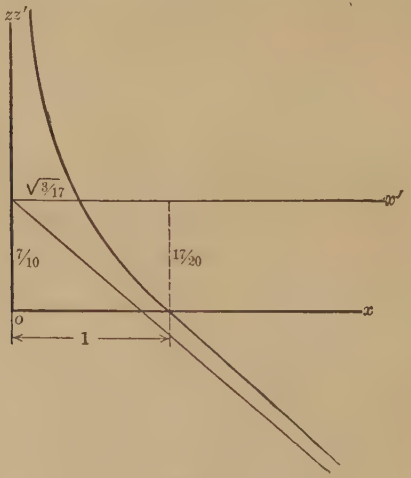


FIG. 6.

If we place $p_H = 1$, then all the pressures will be represented in the figure by distances,

$$P = 1 + z, \quad p_H = 1, \quad p_J = z. \tag{15}$$
$$p_1 = 2(1 - x), \quad p_2 = x, \quad p_3 = z - (1 - x).$$

In the example just treated, the gas mixture does not change its pressure, when the reaction follows by constant volume, nor its volume, when by constant pressure, so long as the temperature remains the same; for from each two volumes (or 2 mols) of the elementary constituents, two volumes of hydrogen iodide are formed. In general, however, by the dissociation of a gas into its gaseous constituents, as also by the reverse process, the volume changes. Thus by the dissociation of nitrogen dioxide

$$N_2O_4 = NO_2 + NO_2;$$

of phosphorous pentachloride,

$$PCl_5 = PCl_3 + Cl_2;$$

of methylether hydrochloride in hydrochloric acid and methylether,

$$(CH_3)_2O.HCl = (CH_3)_2O + HCl;$$

or of carbon dioxide,

$$2CO_2 = O_2 + 2CO,$$

etc.

When from N mols of a substance, N_0 dissociate, each into n mols, then we have

$$N - N_0 + nN_0 = N + (n - 1)N_0 \text{ mols present.}$$

If by this the volume is held unchanged, the pressure P_0 of the original undissociated substance becomes P

in the mixture which results from the dissociation. According to equation (7) (page 68), at temperature θ we have

$$P_0 V = NR_0\theta, \quad PV = [N + (n-1)N_0]R_0\theta.$$

$$\frac{P}{P_0} = 1 + (n-1)\eta, \tag{16}$$

in which the ratio

$$\eta = N_0 : N \tag{17}$$

is designated as the *degree of dissociation.* If we now call the partial pressure exerted by the undissociated portion of the original substance p, and that exerted by each of the n products of dissociation which arise from each molecule p', then

$$P_0 = p + p'; \tag{18}$$

$$P = p + np'; \tag{19}$$

$$\frac{P}{P_0} = \frac{p + np'}{p + p'}, \quad \frac{P - P_0}{P_0} = \frac{(n-1)p'}{p + p'}; \tag{20}$$

and it follows from (16) that

$$\eta = \frac{p'}{p + p'}, \quad p' = \frac{p\eta}{1 - \eta}; \tag{21}$$

$$p = P\frac{1 - \eta}{1 + (n-1)\eta} = P_0(1 - \eta); \tag{22}$$

$$p' = P\frac{\eta}{1 + (n-1)\eta} = P_0\eta. \tag{22b}$$

If by the dissociation instead of holding the volume constant, we keep the pressure so, at P_0 then the volume

changes from V_0 to V, and it follows from the equations

$$P_0V_0 = NR_0\theta, \quad P_0V = [(N + (n-1)N_0]R_0\theta;$$

that for the degree of dissociation we have the relation

$$\frac{V}{V_0} = 1 + (n-1)\eta = \frac{\partial_0}{\partial},$$

where ∂_0 and ∂ represent the densities before and after the dissociation, measured, for example, with respect to atmospheric air. Further, we find

$$\eta = \frac{\partial_0 - \partial}{(n-1)\partial};$$

$$p = P\frac{n\partial - \partial_0}{(n-1)\partial} = P_0\frac{n\partial - \partial_0}{(n-1)\partial};$$

$$p' = P\frac{\partial_0 - \partial}{(n-1)\partial_0} = P_0\frac{\partial_0 - \partial}{(n-1)\partial}.$$

We can also place, by taking ∂' as the density by complete dissociation, i.e., when $\eta = 1$, or

$$\partial' = \partial_0 : n,$$

$$p = Pn\frac{\partial - \partial'}{(n-1)\partial_0} = P_0n\frac{\partial - \partial'}{(n-1)\partial}.$$

From the equations

$$pv = RM\theta, \quad p'V = R'M'\theta$$

we can also find the amount M of the substance, still remaining in the original state, and the amount M' of each of the n equal parts which arise from the dissocia-

tion. R is the specific gas constant of the undissociated substance, and R' is that of one of the products of the dissociation. We find

$$M = \frac{PV(n\vartheta - \vartheta_0)}{R\theta(n-1)\vartheta_0} = \frac{PV}{R\theta} n \frac{(\vartheta - \vartheta')}{(n-1)\vartheta_0}, \quad M' = \frac{PV}{R'\theta} \frac{(\vartheta_0 - \vartheta)}{(n-1)\vartheta_0}.$$

According to the law of dissociation, at the entrance of equilibrium, expression (3) must equal a quantity K, which depends only upon the temperature; thus when all the molecules are of the same kind we have

$$(23) \qquad (np')^n p^{-1} = K, \quad p'n = K' \cdot p,$$

where $K' = K : n^n$ is a new constant. The dependence between p' and p can therefore be shown by a higher parabola, or in the case $n = 2$ by an ordinary one (Fig. 7). The dependence of P and P_0 can then also be seen.

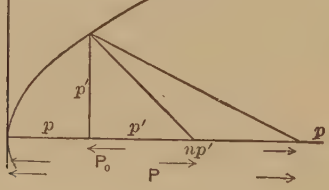


FIG. 7.

Gibbs first proved this theory, in that he showed by decomposition of nitrogen dioxide, N_2O_4, into two molecules of NO_2, that the expression

$$\log p^{-1}(2p')^2 = \log P \cdot 2 \frac{(\vartheta_0 - \vartheta)^2}{\vartheta_0(\vartheta - \vartheta')}$$

was the same as the temperature function in equation (11), page 134, and this expression he calculated from observations by Deville and Troost.

The connection between P and p can also be shown very clearly in the following manner. From (19) and (23) it follows

$$P - p = \sqrt[n]{Kp},$$

$$(P - p)^n = K \cdot p. \tag{24}$$

We recognize easily by the ordinary methods that (24) represents a curve that runs, as is shown by Fig. 8,

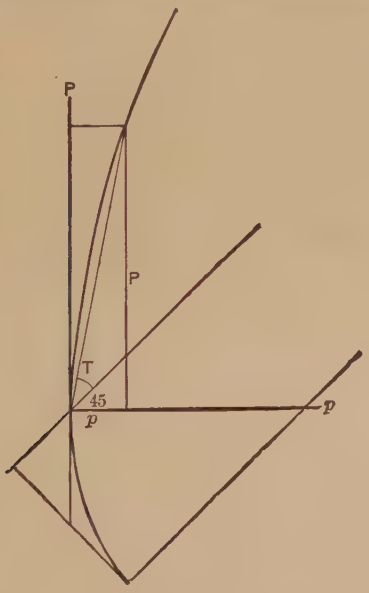


FIG. 8.

at point $p = 0$ in direction of P, and then gradually inclines so that for $p = \infty$ it is at an angle of less than

45° to the p axis. In the case $n = 2$ it is an ordinary parabola, whose axis is inclined at an angle of less than 45° to the p axis. In this case we can also find η from the figure. In equation (22),

$$p = P(1 - \eta) : (1 + \eta),$$

η is the tangent of the angle T, which the radius of the point $(p \,.\, P)$ forms with the direction of the parabola axis.

The dependence of the degree of dissociation η upon the temperature, is given by substitution of (22), and (22*b*) in (23):

$$P_0^{n-1} \,.\, \eta^n = (1 - \eta)K'.$$

When we differentiate the logarithms of both sides we find

$$\frac{n\partial\eta}{\eta\partial\theta} = \frac{\partial lK}{\partial\theta} - \frac{1}{1-\eta}\frac{\partial\eta}{\partial\theta};$$

$$\frac{\partial\eta}{\partial\theta} = \frac{\partial lK}{\partial\theta} \cdot \frac{\eta(1-\eta)}{n(1-\eta)+\eta}.$$

Since η is a pure fraction, $\frac{\partial\eta}{\partial\theta}$ has always the sign of the first factor of the right side, and the degree of dissociation rises and falls with the constant K, whose dependence upon the temperature is apparent from equations (11*b*) and (14*b*), pages 134 and 136. If K rises with the temperature, and if the dissociation between the temperatures θ_1 and θ_2 is nearly complete, then the relation which exists between η and θ has the form given in Fig. 9.

The course of the dissociation of carbon dioxide into oxygen and carbon monoxide,

$$2CO_2 = 2CO + O_2,$$

has been investigated by Le Chatelier. The exchange numbers (umsatz zahlen) of the three constituents are

$$\nu_1 = -2, \quad \nu_2 = 2, \quad \nu_3 = 1;$$

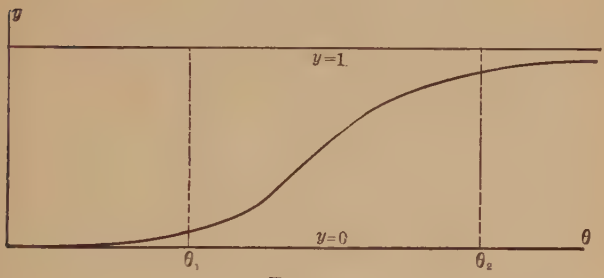


FIG. 9.

and for the partial pressures, which we will designate by p_1, p_2, p_3, we have

$$P = p_1 + p_2 + p_3,$$

where P is the total pressure.

Further, when only CO_2 is present at first

$$p_2 = 2p_3.$$

Since here 2 molecules fall into 3, for use of equations (16) to (23) we must place

$$n = 3/2, \quad p' = 2p_3 = p_2, \quad p = p_1.$$

And the degree of dissociation is given by help of equation (21) as:

$$\eta = \frac{p_2}{p_1 + p_2}.$$

Further, we find

$$2p_3 = p_2 = P\frac{2\eta}{2+\eta}, \quad p_1 = P\frac{2(1-\eta)}{2+\eta}.$$

By this equation (11*b*), page 134, goes over into the form

$$l\left(\frac{2+\eta}{2(1-\eta)}\right)^2\left(\frac{2\eta}{2+\eta}\right)^2\left(\frac{\eta}{2+\eta}\right)P = -\frac{E_0}{R_0\theta} + \frac{C_p}{R_0}l + A.$$

$$l\left(\frac{\eta^3}{(2+\eta)(1-\eta)^2}\right) = \frac{C_p}{R_0}l\theta - lP - \frac{E_0}{R_0\theta} + A.$$

If we now calculate a table giving for the values $\eta = 0$ to $\eta = 1$, the logarithms, and conversely for each value of the latter, the corresponding value η, then for each pressure P, and each temperature θ, the degree of dissociation, η, can be found. We must observe, however, (1) the specific heats of the three constituents by constant pressure, from which by equation (6), p. 133, the value C_p follows; (2) the heats of reaction Q, for any determined temperature θ, by constant pressure, from which, according to

$$Q = E_0 + C\theta$$

(see derivation of equation (14), p. 135), the constant E_0 is obtained; (3) a single value of η, which is given by a certain θ and P,—in order to be able to calculate the constant A. The values chosen by Le Chatelier are, for many reasons, to be objected to; but here we have not space to enter into this interesting subject any further, but must reserve it for a future opportunity.

We will not give here an example for equation (14) on account of the lack of experimental data, although wide applications have been made of it in technical subjects.

If an electrolyte dissociates into its ions, as according to the hypothesis of Arrhenius is the case with solutions, its degree of dissociation $\eta = \mu : \mu\infty$ (see page 109) gives the concentration of each ion. If there are n mols of the electrolyte in solution, then there are ηn mols of each ion present and $(1 - \eta)n$ remains undecomposed. If n_0 is the number of mols of the solvent, then, since the exchange numbers (umsatz zahlen) of the ions are $+1$ and that of the electrolyte -1, the expression

$$\left(\frac{\eta n}{n_0 + (1+\eta)n}\right)\cdot\left(\frac{\eta n}{n_0 + (1+\eta)n}\right)\cdot\left(\frac{(1-\eta)n}{n_0 + (1+\eta)n}\right)^{-1} = K'$$

must depend only upon the temperature and pressure. If the solution is highly diluted, i.e., n_0 very large as compared to n, it follows that

$$\frac{\eta^2}{1-\eta}\frac{n}{n_0} = K'.$$

Finally, we can place $\frac{n_0}{n}$ proportional to the dilution v, i e., the volume to which 1 gram or 1 mol of the salt is brought: Or

$$\frac{\eta^2}{(1-\eta)v} = K. \tag{25}$$

From this the term η can be found by solving the equation

$$\eta^2 + K\eta v - Kv = 0,$$

or

$$\eta = \frac{Kv}{2}\left\{\sqrt{\frac{4}{Kv}} + 1 - 1\right\}.$$

The dependence between the degree of dissociation y and the dilution v is represented by a hyperbola which in the origin touches the y axis (Fig. 10).

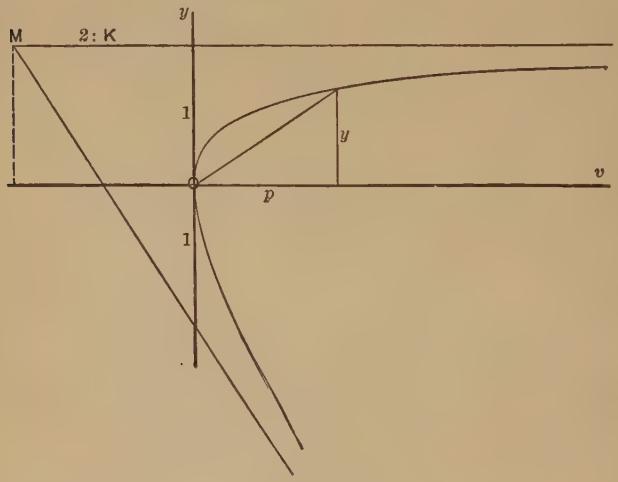


FIG. 10.

The formula is supported by numerous investigations, e.g., by the following series from van't Hoff and Reicher. For acetic acid at 19°.1, η is the ratio of the molecular electrical conductivity, to that at infinite dilution, i.e., by complete dissociation. By the dilution of a gram molecule (mol) of acetic acid to

$$9.269l \quad 4- \quad 16- \quad 64- \quad 256- \quad 1024 \times 9.269l$$

the molecular conductivity referred to mercury was

$$4.69 \quad 9.38 \quad 18.6 \quad 35.9 \quad 67.4 \quad 122 \times 10^{-7}$$

Since at infinite dilution the molecular conductivity is 335×10^{-7}, the degrees of dissociation, are in parts per hundred,

$$100\eta = 1.40 \quad 2.80 \quad 5.55 \quad 10.7. \quad 20.1 \quad 36.4.$$

From equation (25) the values of $\log K$ follow; they have the characteristic -5, and the mantissas are

$$331 \quad 337 \quad 342 \quad 335 \quad 329 \quad 341$$

The value of K is thus actually independent of η and v.

If we take instead of the degree of dissociation η, the ratio of the molecular conductivity μ, to the corresponding value μ_∞ for infinite dilution, and then instead of μ the specific conductivity $\sigma = \mu n$, i.e.,

$$\eta = \frac{\mu}{\mu_\infty} = \frac{\mu n}{\mu_\infty n} = \frac{\sigma}{\mu n_\infty},$$

the equation $n\eta^2 : (1 - \eta) = K' n_0$ goes over into the form

$$\sigma^2 + n_0 \mu_\infty K' \sigma - n_0 K' \mu^2{}_\infty n = 0,$$

or

$$(\sigma + \tfrac{1}{2} n_0 K' \mu_\infty)^2 = K' n_0 \mu^2{}_\infty (n + \tfrac{1}{4} n_0 K').$$

The relation between n and σ is also represented by a parabola, which cuts the n axis at the origin at an angle, whose tangent is μ_∞. In fact the observations of *F. Kolrausch* show such a behavior at high and

medium dilutions. That the formula is not applicable to concentrated solutions is shown by its derivation.

If a solid body decomposes by heating into several gases, then we must apply the equations on pages 134 and 136 to the solid as well as the gaseous phases. Since, however, the concentration of the solid is 1, the gas mixture only comes into further consideration. Ammonium carbimate, for example, dissociates into carbon dioxide and ammonia according to the formula

$$NH_4O \cdot CO \cdot NH_2 = CO_2 + 2NH_3.$$

If p is the partial pressure of the carbon dioxide, p_2 that of the ammonia, then

$$p_1 p_2^2 = K,$$

a quantity which changes only with the temperature. If the total pressure is produced only by the products of the decomposition, whose partial pressures in this case are p_1' and p_2', then

$$P = p_1' + p_2', \quad p_2' = 2p_1'.$$
$$\therefore \quad p_1' = \frac{P}{3}, \quad p_2' = \frac{2P}{3}, \quad K = \frac{4P^3}{27}.$$

If, however, in the space where the decomposition takes place there is, before the dissociation begins, beside the carbimate, still ammonia or carbon dioxide, then the process goes on until the entrance of equilibrium, which fulfils, as before, the equation

$$p_1 p_2^2 = \frac{4P^3}{27},$$

where $P = p_1 + p_2$ again represents the total pressure, which is only dependent upon the temperature. This consequence of the theory has been proved by Isambert. He observed at 34°.0 C., with a total pressure of 17.0 mm. mercury, the different partial pressures by different (initial) excesses of ammonia, or of carbon dioxide, and found for $\sqrt[3]{\frac{2^2}{4^1} p_1 p_2^2}$, instead of 17.0, the values

17.0 16.5 16.7 18.1

At 42°.5 C., with a total pressure of 28.8 mm., he found for each cubic foot, by different initial states the numbers

28.9 28.4 28.6 29.2

On the other hand, the action of an indifferent gas added to the system was entirely different. If its partial pressure is p_0, then, by formula (3),

$$p_0 p_1 p_2^2 = K = \frac{4P^3}{27}, \quad P = p_0 + p_1 + p_2;$$

i.e., it is without influence upon the ratio of p_1 and p_2.

If n mols of alcohol are mixed with 1 mol of acetic acid, acetic ester and water are formed by a very slow reaction, which is represented by the equation

$$CH_3COOH + C_2H_5OH \rightleftarrows CH_3COOH_5C_2 + H_2O.$$

After conclusion of the reaction all four substances are present. If x molecules have reacted, and if at first there was neither water nor ethylacetate present, then, according to equation (5),

$$\frac{(n - x)(1 - x)}{x^2}$$

must be constant in value, and, according to observation, equal 1/4. From

$$4(n - x)(1 - x) = x^2$$

it follows, since to the value $n = 0$ the value $x = 0$ corresponds,

$$x = \tfrac{2}{3}(n + 1) - \sqrt{n^2 - n + 1}.$$

By this we find

for $n =$	0.05	0.20	0.50	1.0	2	4	8	5.00
$x =$	0.05	0.19	0.42	0.67	0.85	0.93	0.95	1.00

while Berthelot and Péan de St. Gilles observed

$x =$	0.05	0.19	0.43	0.67	0.84	0.90	0.97	1.00

Further examples can be found in:

Ostwald, Lehrbuch der allgem. Chem., 2d ed. vol. 2, 1887.

Nernst, Theoretical Chemistry. Trans. by Dr. Palmer.

Le Chatelier, Recherches expérimentales et théoriques sur les équilibres chimiques. Paris, 1888. Also in Annales des mines, 1888.

van't Hoff, Études de dynamique chimique. Amsterdam, 1884.

CHAPTER IV.

FREEZING AND BOILING POINTS; ALSO VAPOR PRESSURES OF HIGHLY DILUTED SOLUTIONS.

In a closed space there is a solution and its vapor. If n mols of solvent are in the solution and n' in vapor, and if, further, n_1 mols of the dissolved substance, or salt, are in the solution and n_1' in the vapor, then according to (eq. 9), page 69, the concentrations in the liquid phase are $n : (n + n_1)$ and $n_1 : (n + n_1)$, and in the gaseous one are $n' : (n' + n_1')$ and $n_1' : (n' + n_1')$. According to (eq. 21), page 123, the chemical intensities are

$$(1)\quad \begin{cases} \Pi = \Pi^* + R\theta l\dfrac{n}{n+n_1}, & \Pi_1 = \Pi^* + R_1\theta l\dfrac{n_1}{n+n_1}, \\ \Pi' = \Pi'^* + R'\theta l\dfrac{n'}{n'+n_1}, & \Pi_1' = \Pi_1'^* + R_1\theta l\dfrac{n_1'}{n'+n_1}, \end{cases}$$

provided that only reversible processes are taken into consideration. Here θ means the temperature of all parts of the system, the quantities with stars (*) are the intensities that would be shown by the concentration 1, and the constant R is related to the gas constant $R_0 = 2$ cals in such a way that

$$(2)\qquad mR = m'R' = m_1R_1 = m_1'R_1' = R_0,$$

where m, m', m_1, and m_1' are the molecular weights.

Now by the law proven on page 117 a system is in equilibrium when

$$\Pi = \Pi', \quad \Pi_1 = \Pi. \tag{3}$$

The pure solvent might be in equilibrium with its vapor, at the temperature θ, when its pressure is p_0, while the solution considered might be in the same state at pressure p. Conversely, by this pressure, p, the pure solvent would not boil at the temperature θ, but at θ_0.

We will confine our further treatment to highly diluted solutions. We call a *highly diluted solution* one in which the chemical intensity of the solution differs from that of the pure solvent, only by terms which contain the first powers of the concentration and temperature or pressure. If, for example, we develop Π by Taylor's series, as a function of the vapor tension, p, and the number, n_1, of mols dissolved,

$$\Pi = \Pi_0 + \left(\frac{\partial \Pi}{\partial p}\right)_0 (p - p_0) + \left(\frac{\partial \Pi}{\partial n_1}\right)_0 n + \text{higher powers}, \tag{4}$$

where the terms with the index 0 are the values of the intensities 3 and their differential quotients, for $p = p_0$ and $n_1 = 0$; then for highly diluted solutions we can neglect the higher powers, and leave the equation as above. In the same way,

$$\Pi' = \Pi_0' + \left(\frac{\partial \Pi'}{\partial p}\right)_0 (p - p_0) + \left(\frac{\partial \Pi'}{\partial n_1'}\right) n_1'. \tag{4b}$$

Since now the pure solvent ($n_1 = 0$), at the pressure $p = p_0$, is in equilibrium with its vapor, then

$$\Pi_0 = \Pi_0'. \tag{5}$$

and we obtain, by aid of (3),

$$(6)\quad \left(\frac{\partial \Pi'}{\partial p} - \frac{\partial \Pi}{\partial p}\right)_0 (p - p_0) = \left(\frac{\partial \Pi}{\partial n_1}\right)_0 n_1 - \left(\frac{\partial \Pi_1}{\partial n_1'}\right)_0 n_1'.$$

The differential quotients on the left side, according to (eq. 26), page 125, are equal to the specific volumes, v_0, v_0', of the pure solvent and its vapor at the pressure $p = p_0$; those on the right follow from eq. (1). We obtain

$$(7)\quad (v_0' - v_0)(p - p_0) = -\frac{R\theta_0}{n + n_1} n_1 + \frac{R'\theta_0}{n' + n_1'} n_1'.$$

If the salt in the vapor of the solution is unnoticeable (i.e., n_1' very small without R'—in consequence of strong dissociation of the solvent by evaporation—being very large), and if, further, the specific volume of the liquid is negligibly small, as compared to its vapor, then this above relation becomes simplified to

$$(8)\quad v_0'(p_0 - p) = \frac{n_1}{n_1 + n} R\theta_0 = C_1 R\theta_0,$$

where C is the concentration of the salt in the solution.

This formula (in which strictly v_0' should be substituted by equation (7), page 81, has been proven extensively only in an altered form. If the vapor of the pure solvent follows the equation of state of perfect gases, then

$$(9)\quad p_0 v_0' = R'\theta_0.$$

Since, however, R' can only vary from R when the

solvent dissociates by evaporation, which possibility we can here exclude, we can place

$$\frac{p_0 - p}{p_0} = \frac{n_1}{n + n_1} = C_1 \tag{10}$$

In this equation we find expressed the law deduced experimentally by Raoult in 1887, which reads: *A solution boils at a lower pressure than the pure solvent; the ratio of the lowering of the vapor tension to the vapor tension of the pure solvent, the so-called "relative" lowering of the vapor tension, is equal to the concentration of the solution.*

Finally, by a simple alteration of equation (10) we can derive the formula

$$\frac{p_0 - p}{p} = \frac{n_1}{n}. \tag{10b}$$

Since p does not differ from p_0, we can formulate the law as follows: *The "relative" lowering of the vapor tension, is equal to the ratio of the number of mols dissolved, to the number of mols of the solvent.*

In equation (4) the intensity was treated as a function of the pressure and number of mols dissolved. Since, however, the pressure of a saturated vapor depends only upon the temperature, we can also look upon the intensity as a function of the temperature and the number of mols dissolved, and place

$$\begin{cases} \Pi = \Pi_0 + \left(\frac{\partial \Pi}{\partial \theta}\right)_0 (\theta - \theta_0) + \left(\frac{\partial \Pi}{\partial n_1}\right)_0 n_1; \\ \Pi' = \Pi_0 + \left(\frac{\partial \Pi'}{\partial \theta_1'}\right)_0 (\theta - \theta_0) + \left(\frac{\partial \Pi'}{\partial n_1'}\right) n_1. \end{cases} \tag{11}$$

By aid of equations (3) and (5) it follows, further, that

$$(12)\quad \left(\frac{\partial \Pi'}{\partial \theta} - \frac{\partial \Pi}{\partial \theta}\right)_0 (\theta - \theta_0) = \left(\frac{\partial \Pi}{\partial n_1}\right)_0 n_1 - \left(\frac{\partial \Pi'}{\partial n_1'}\right) n_1';$$

and according to equation (26) (page 125) we obtain

$$(13)\quad (s_0'' - s_0')(\theta - \theta_0) = \frac{R\theta_0}{n + n_1} n_1 + \frac{R'\theta_0}{n' + n_1} \cdot n_1',$$

where s_0 and s_0' represent the entropies of the unit of mass of the pure solvent and its vapor. We substitute for these entropies the heat of evaporation Q_0 for 1 mol, m, of the pure solvent. According to the conception of entropy, and under the restriction that no dissociation takes place by evaporation,

$$(14)\quad Q_0 = m\theta_0(s_0' - s_0)$$

$$Q_0(\theta - \theta_0) = \frac{n_1}{n + n_1} R_0\theta_0^2,$$

$$(15)\quad \frac{Q_0}{R_0\theta_0^2}(\theta - \theta_0) = \frac{n_1}{n + n_1} = C_1,\ \theta - \theta_0 = \frac{R_0\theta_0^2}{Q_0} C_1,$$

where, if n_1 is very small as compared to n, we can place

$$(15b)\quad \frac{Q_0}{R_0\theta_0^2}(\theta - \theta_0) = \frac{n_1}{n},\quad \theta - \theta_0 = \frac{R_0\theta_0^2}{Q_0} \frac{n_1}{n}.$$

The above development of equation (15) is for the case of the evaporation of a solution. But all the conclusions hold as well, for the case that a phase separates out of the solution in any other form than a gaseous one; thus for freezing, provided only that the solid body separating out is the pure solvent, or at

most contains a negligible amount of the salt. While Q_0, in the case of evaporation, is positive, it is negative in case of freezing.

We can therefore express equation (15) in words as follows: *A solution has a higher boiling-point and lower freezing-point than the pure solvent; this temperature difference* $(\theta - \theta_0)$ *is proportional to the concentration of the salt. The proportional factor,* $R_0\theta_0^2 : Q_0^c = f$, *increases with the square of the temperature* (θ_0^2), *and decreases by increasing heat of aggregation.* The value of σ is generally derived from observations of the specific increase of the boiling-point, or from the specific decrease of the freezing-point. (The specific change is the change of temperature shown by a 1% solution, i.e., where $mn = 100m_1n_1$). If we place the heat of aggregation as referred to one gram, $Q_0 : m = q_0$, and $R_1m_1 = R_0$, then

$$\sigma = \frac{R_1\theta_0^2}{100q_0} = \frac{mR_0\theta_0^2}{100m_1Q_0} = \frac{mf}{100m_1}.$$

The m_1 multiple of this, the *molecular* increase of the boiling- or decrease of the freezing-point, μ, is often given in place of σ,

$$\mu = \frac{R_0\theta_0^2}{100q_0} = \frac{mf}{100}.$$

The laws (10) and (15) were discovered by Raoult (1883) and van't Hoff, and are important to experimental chemistry, as a means of finding the molecular weight of a substance in solution, which often differs

from that in other states.* The method of using them will be apparent from the following examples:

According to the results of Raoult, 11.346 grams of oil of turpentine, $C_{10}H_{16}$, molecular weight 136, dissolved in 100 grams of ether $(C_2H_5)_2O$, molecular weight 74, gives a solution that boils at a pressure of 36.01 cm. of mercury, while pure ether shows a vapor pressure of 38.30 cm. It follows, therefore, that the relative lowering of the vapor pressure (left side of equation (10) $\frac{p_0 - p}{p_0}$) is

$$\frac{2.29}{38.30} = 0.0598.$$

On the other hand, we know that 11.346 : 136 = 0.0834 mols are dissolved in 100 : 74 = 1.351. The concentration is therefore $\left(\frac{n_1}{n + n_1}\right)$

$$\frac{0.0834}{1.434} = 0.0582.$$

If the molecular weight is to be derived from the observation, then we must find the number of mols dissolved from equation (10*b*),

$$\frac{2.29}{36.01} \cdot 1.351 = 0.0859,$$

---

* See Windisch, Die Bestimmung des Molecular-Gewichts (Berlin, 1892).

and from this the molecular weight,

$$11.346 : 0.0859 = 132.$$

Beckmann gives the boiling-point of carbon disulphide, CS_2, as 46°.2 C.; the heat of evaporation for one gram is, according to Regnault, 84.82. From this the proportional factor f is found to be

$$\frac{R_0\theta_0^2}{Q_0} = \frac{2 \times 319.2^2}{76 \times 84.82} = 2400 : 76 = 31.6.$$

It is a function of the boiling temperature; for example, at pressure,

257 760 1841 mm. of mercury,

or boiling temperature,

16.2 46.2 76°.2 C.,

the molecular increase of the boiling-point is

18.9 24.0 30.4

From Beckmann's observations, 1.4475 gr. of phosphorus in 54.65 gr. of carbon disulphide boils at a temperature 0°.486 higher than the pure solvent, it follows now from the approximate formula (15*b*) that the number of mols dissolved is

$$\frac{0.486}{31.6}\frac{54.65}{76} = 0.0111,$$

and the molecular weight is $1.4475 : 0.0111 = 130$, so that $P_4 = 124$ represents a molecule. From the molecular weight 124, the number of mols would be 0.0117, and the increase of the boiling-point 0°.514 C. follows.

From an observation by Arrhenius a water solution of sodium chloride, which contains 0.273 gr. NaCl in 100 ccm. H_2O, freezes at $-0°.177$ C. The molecular lowering of the freezing-point of water solutions is

$$\frac{2.273^2}{100 \times 79 \times 87} = 18.66.$$

If N_1 is the number of mols of salt in 100 cc., we find

$$N_1 = \frac{0.177 \cdot 100}{1866} = 0.0095,$$

while 0.273 gr., at the molecular weight 58.5, would give 0.0047 as the number of mols dissolved. The NaCl must therefore be looked upon as almost completely dissociated, in this water solution, into $\overset{+}{Na}$ and $\bar{Cl}$.

A very much stronger solution of 3.155 gr. NaCl in 100 cc. H_2O showed a freezing-point of $-1°.894$. It follows that

$$N_1 = \frac{1.894 \cdot 100}{1866} = 0.102$$

is the number of mols in 100 cc., while the molecular weight 58.5 would lead to $3.155 : 58.5 = 0.054$. In this case the salt is not completely dissociated.

If the degree of dissociation (see pages 109 and 110) is η, we find that instead of N' molecules we have

$$N_1 = N'(1 - \eta) + N' n'\eta,$$

when each dissociating molecule separates into n' molecules. The ratio of the number thus found to be present, to the number that would be present if there

were no dissociation is $N_1 : N' = j$, and we have

$$j = 1 + (n' - 1)\eta.$$

In the above example $n' = 2, j = 0.102 : 0.054 = 1.89, \eta = 0.89$.

Notwithstanding that it is the first idea in our presentation of physical chemistry, to derive the natural phenomena from the general subject of energetics, still we cannot omit the general theoretical relations which exist between the single phenomena independent of that foundation principle of all. When we see how the single facts mutually support one another, the value of the great principle underlying them all will be recognized. Besides this, it follows from the fact that from one the others may be derived, that the phenomenon is also given with an equal degree of accuracy.

Of the two equations (10) and (15), that concern the evaporation of salt solutions, the one is a mathematical consequence of the other. If we represent the vapor pressure p of a solution, as a function of the temperature θ, and plot it as a curve for the pure solvent, we obtain Fig. 11. We obtain for the concentration O, as well as for any other concentration C_1, of the salt another curve for the vapor pressure; p is here a function of θ and C_1. Neglecting the higher powers, Taylor's series gives

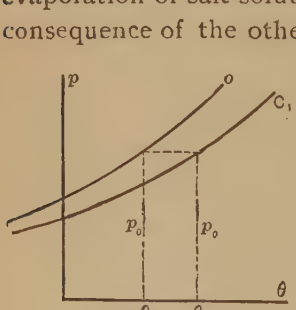


FIG. 11.

$$p(\theta, C) = p(\theta_0, O) + \left(\frac{\partial p}{\partial \theta}\right)_0 (\theta - \theta_0) + \left(\frac{\partial p}{\partial C_1}\right)_0 C_1.$$

In order that the solution may boil at the same pressure as the pure solvent, for example, at atmospheric pressure, it is necessary that

$$\left(\frac{\partial p}{\partial \theta}\right)_0 (\theta - \theta_0) = -\left(\frac{\partial p}{\partial C_1}\right)_0 C_1.$$

According to (10) the right side is $p_0 . C_1$, and according to (14), page 91, the left side can be rearranged. We find

$$\frac{Q_0}{R_0 \theta_0^2} p_0 (\theta - \theta_0) = p_0 C_1,$$

$$\frac{Q_0}{R_0 \theta_0^2} (\theta - \theta_0) = C_1,$$

i.e., equation (15).

This consideration for the process of evaporation could be carried over to that of freezing, if the functions of the temperature in the figure were chemical intensities; then the above development would lead also to (15) as applied to the process of freezing.

But here the functions are vapor pressures; a solution as well as the solvent has the same vapor pressure when boiling—the atmospheric pressure, for example; by freezing of the solution, however, the partial pressure of the vapor does not necessarily agree with that of the pure solvent by freezing. These two pressures are related in another manner: they belong to the curve of vapor pressure of the solid phase which separates out by freezing.

If first we imagine water, and then ice, at the tem-

perature θ, transformed into vapor, and if we distinguish the two curves of vapor pressure (Fig. 12) by

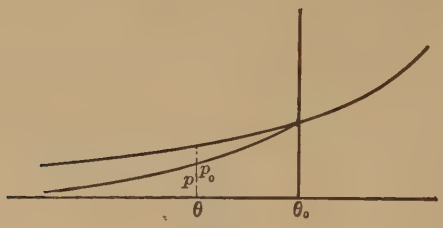


FIG. 12.

the indices w and i, then, by use of equation (14), page 91, in both cases, and by subtraction of the heat $-Q_0$ (that is necessary to change 1 mol of ice into water), we find

$$-Q_0 = R_0\theta_0^2\left\{\left(\frac{\partial p}{\partial\theta}\right)_i - \left(\frac{\partial p}{\partial\theta}\right)_w\right\}\frac{1}{p_0'},$$

where p_0' is the pressure of the vapor at $\theta_0°$. $-Q_0$ is used in order to bring the sign the same as it was above. Now by Taylor's series, neglecting higher powers,

$$p_0 = p_0' + \left(\frac{\partial p}{\partial\theta}\right)_w(\theta - \theta_0), \quad p = p_0' + \left(\frac{\partial p}{\partial\theta}\right)_i(\theta - \theta_0).$$

Here p_0 is the vapor pressure of water, and p that of ice at $\theta°$. If now $\theta°$ is the freezing-point of the solution, then p is also the vapor pressure of the solution at freezing. The equations give

$$p_0 - p = (\theta - \theta_0)\frac{Q_0}{R_0\theta_0^2}p_0',$$

a formula which, by neglecting the small difference between p_0' and p, corresponds to equation (15*b*), since from (10*b*) we have the relation

$$\frac{p_0 - p}{p} = \frac{n_1}{n};$$

CHAPTER V.

OSMOTIC PRESSURE.

Up to the present, all parts of the systems considered have been restricted by the condition, that equilibrium can only be present when the pressure of the whole system is the same. It is possible, however, to realize conditions by which the possibility of chemical action is present, as in the ones already discussed, and by which even after entrance of equilibrium the pressure of the single parts is different and remains so. Gravity causes, for example, in a column of vapor of considerable height, differences in pressure of that kind. If two substances, for example a solution and the pure solvent, give the same vapor, at the same temperature, under different vapor pressures, it is possible, when the two substances are near one another in a closed space, for equilibrium to be present only after their surfaces have stopped at different height, which is caused by their unequal evaporation. It is only when the difference in height of the evaporating surfaces is equal to their difference of vapor pressure that equilibrium can be reached.

The chemical intensity of each constituent must

also in such a case be the same, as an examination according to the conclusions reached on pages 115 and 116 will show.

Experimentally such differences of pressure can be made by means of semi-permeable cells, as *Graham* used, and as Pfeffer has so carefully and completely studied. They are of great importance; some substances can go through them, while others are prevented. In other words, on both sides of such a partition the chemical intensities of certain substances are equal when equilibrium has been established; while the chemical intensities of other substances do not equalize at all and yet equilibrium is present. If on both sides of a semi-permeable partition there is a solvent which can pass through it readily, and if we replace that on one side by a dilute solution of a salt, which cannot pass through it, then the intensity of the solvent in the solution must be just as great as in the pure state.

We will derive this from the equation of energy for the solution and for the pure solvent. For the solution we have

$$(1) \qquad dE \leqq \theta dS - PdV + \Pi dM + \Pi_1 dM_1$$

and for the solvent

$$(2) \qquad dE_0 \leqq \theta dS_0 - P_0 dV_0 + \Pi_0 dM_0.$$

P and P_0 are the pressures, V and V_0 the volumes, S and S_0 the entropies, E and E_0 the energies of the

two bodies on the two sides of the semi-permeable partition, θ their common temperature, Π_0 the chemical intensity of the pure solvent, M_0 its mass, Π and M the corresponding values for the solvent in which the salt is dissolved, and Π_1 and M_1 the intensity and mass of this substance. If now the two phases form an isolated system, as it must when equilibrium is established, then according to pages 115, 116, and 117, or also page 77,

$$(3)\quad dE + dE_0 = 0, \quad dS + dS_0 = 0, \quad dM + dM_0 = 0.$$

Further, none of the volumes can change without volume energy being given out or absorbed; therefore

$$(3b)\qquad dV = 0, \quad dV_0 = 0,$$

and the nature of the half-porous partition requires that

$$(3c)\qquad dM_1 = 0.$$

Hence the addition of the above energy equations gives us

$$(4)\qquad 0 \leqq (\Pi - \Pi_0) dM_0;$$

and since dM_0 can be positive or negative,

$$(4b)\qquad \Pi = \Pi_0.$$

The intensity is, however, a function of the concen-

tration and pressure. If the concentration of the solution is

$$C = \frac{n}{n + n_1}, \tag{5}$$

where n is the number of mols of the solvent, n_1 that of the salt. If P is the pressure on the side of the solution and P_0 that on the side of the pure solvent, then according to Taylor's theorem the intensity of the solvent in the solution is

$$\Pi = \Pi_0 + \left(\frac{\partial \Pi}{\partial P}\right)_0 (P - P_0) + \left(\frac{\partial \Pi}{\partial C}\right)_0 (C - 1), \tag{6}$$

where Π_0 is the intensity of the pure solvent to which the terms with the index o refer. Higher powers are neglected since the solution is assumed to be very dilute. (If this latter were not the case we would have

$$d\Pi = 0 = \frac{\partial \Pi}{\partial P} \cdot dP + \frac{\partial \Pi}{\partial C} \cdot dC.) \tag{6b}$$

Since now the two intensities are equal,

$$\Pi = \Pi_0,$$

it follows by aid of equation (26), page 125, and equation (21), page 123, from equation (6),

$$v(P - P_0) = \frac{R_0 \theta}{mC} C_1. \tag{7}$$

$C - 1 = - n_1 : (n + n_1) = - C_1$, where C_1 is the concentration of the salt in the solution. Here v equals the specific volume, m the molecular weight of the solvent, θ the absolute temperature, and R_0 the gas con-

stant of nearly 2 cals. We can bring in still the volume of a mol of the dissolved substance, v_m, so that

$$n_1 \cdot v_m = v \cdot m \cdot n, \tag{8}$$

and obtain

$$\begin{cases} (P - P_0)\, mv = R_0\theta \cdot \frac{n_1}{n}, \\ (P - P_0)\, v_m = R_0\theta. \end{cases} \tag{9}$$

The difference of pressure $P - P_0$, by which the solution is stronger than the solvent, i.e., the *osmotic pressure* of the solution, depends upon the temperature and the volume, which the dissolved substance occupies, according to the same laws, *as if the latter was in the state of a perfect gas.* This law, which was discovered by van't Hoff, is sustained by experiment.

Pfeffer observed that a 1% sugar solution, by use of a membrane of copper ferrocyanide, at a temperature of 15°.C., gave a difference of pressure against water of 0.684 atmosphere. Since a mol of raw sugar, $C_{12}H_{22}O_{11}$, weighs 342 grams, then

$$0.684 \cdot 1033.3 \cdot 34{,}200 = 288.5\, R_0$$

is to be substituted, from which follows

$$R_0 = 83{,}800 \text{ g*cm.} : {}^\circ\text{C.} = 1.94 \text{ cals.} : {}^\circ\text{C.}$$

The observation that at 0° a 1% sugar solution shows a pressure of 49.3 cm. of mercury leads to $R_0 = 84{,}200$ or 1.96.

A mol in a liter would, according to this, at 0°, exert a pressure of

$$\frac{1.96 \times 273}{1000 \times 1033.3} = 22 \text{ atmospheres},$$

whether the substance was dissolved or not.

From the laws of osmotic pressure, by an approximate calculation, we find the laws for the lowering of the vapor pressure of a dilute solution. A vessel A, closed at the bottom with a semi-permeable partition (Fig. 13), contains a solution, and its lower part is placed in another vessel B, in which there is the pure solvent. The whole stands in a closed space C that is filled with the vapor of the solvent. This vapor shows on the surface of the solution the pressure p, on the surface of the outer vessel the pressure p_0. If the solution, at the establishment of equilibrium, is h cm. higher than the solvent from which it is separated by the semi-permeable film, then, according to the well-known law of the equilibrium of gaseous bodies,

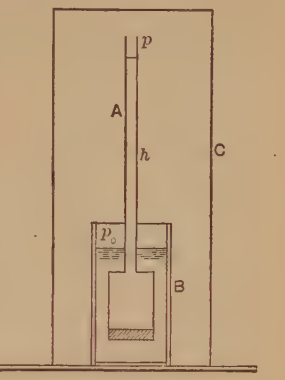


FIG. 13.

$$-dp = s \,.\, dh = \frac{dh}{v}, \tag{10}$$

when s is the specific gravity and v the specific volume of the vapor. If this vapor follows the laws of Mariotte and Gay-Lussac, and if m_0 is its molecular weight, then we have further

$$-\frac{dp}{p} = \frac{m_0}{R_0\theta}dh; \tag{11}$$

$$l\frac{p_0}{p} = \frac{m_0}{R_0\theta}h; \tag{11b}$$

On the other, hand the osmotic pressure is now equal to the difference of vapor pressures increased by the pressure of a column of the liquid of the height h. If the difference in specific weight of the two can be neglected and the specific weight of the solution, which strictly is $(nm + n_1 m_1) : n_1 v_m$, can be called $nm : n_1 v_m$, we obtain

$$P - P_0 = p + h\frac{nm}{n_1 v_m} - p_0. \tag{12}$$

It therefore follows, when we also neglect the pressure of the column of vapor $p - p_1$, as compared to that of the column of liquid, from equation (9), since $m = m_0$,

$$h\frac{n}{n_1} m_0 = R_0 \theta. \tag{13}$$

We obtain by use of equation (11*b*)

$$\frac{n}{n_1} l\frac{p_0}{p} = 1. \tag{14}$$

If now p and p_0 are but slightly different, as is the case with dilute solutions, we can place

$$l\frac{p_0}{p} = l\left(1 + \frac{p_0 - p}{p}\right) = \frac{p_0 - p}{p},$$

and we find

$$\frac{p_0 - p}{p} = \frac{n_1}{n}; \tag{15}$$

i.e., equation (10*b*), page 164.

The osmotic pressure has obtained a very prominent theoretical place in physical chemistry, since it was used by van't Hoff in order to make clear the relation of chemical substances. According to the foregoing book, the chemical intensity, which was introduced by Gibbs, leads to a more general method of treating chemical phenomena. The theory should not stop at the osmotic pressure, but should reach further back still to the *intensities*. Of the relation of osmotic pressure to intensity we can predict only for very highly diluted solutions. From equation (21), page 123, it follows that the chemical intensity Π_1 of a constituent in highly diluted solutions, is related to the osmotic pressure of the solution, as against that of the pure solvent by the formula

$$\Pi_1 = A_1 + R_1\theta l(P - P_0),$$

where A_1 is a function of pressure and temperature, and R_1 is the specific gas constant of the constituent.

CHAPTER VI.

DIFFUSION.

In the previous chapters we have studied the equilibrium of chemically different substances. Before, however, equilibrium is established changes of energy take place, and these characteristic quantities of the system are functions of the time. The investigation of these *changes, during a certain interval of time*, still remains to be considered.

In mechanics those changes of energy which depend upon the time are classed under a special form of energy, i.e., kinetic energy. In like manner the changes in a system, in whose different phases the same constituent has a different intensity, can also be considered under this heading of kinetic energy. In fact we always find movements in such a system, and sometimes very powerful ones. In particular we must ascribe to kinetic energy, the decrease of the intrinsic energy for non-reversible processes, by which the function of quantity (entropy, volume, and mass) remains unchanged. The standpoint of every molecular hypothesis is that the kinetic energy of the motion is the immediate cause of the chemical reaction, and the phenomenon of motion, shown by chemical processes,

has thus been the principal source of these hypotheses.

However, this has not proved favorable for the mathematical treatment of the subject. In the cases where kinetic energy has been exerted upon the surroundings it has proven more to the point to carry the chemical investigation to the establishment of an "overpressure" (überdruck); or in other words, to look upon the consequence of the chemical reaction as a pressure energy, the calculation of which into kinetic energy is then possible by means of the principles of dynamics. The osmotic pressure can serve as a good illustration of this method.

In many cases, however, no kinetic energy is given out by the system, and in others so little as to be unnoticeable, as compared with the other forms of energy, especially heat; this fact has led, in the molecular hypothesis, to the assumption of internal friction.

These cases of motion are always shown, by the increase of one phase, at the cost of another, as in the change of place of a phase in the system.

The simplest case of this is the motion of a soluble salt in its solvent. We possess no other mathematical grasp of this process than that offered by *Fick's law of diffusion.* From the conception of chemical intensity we arrive at this law, which was deduced experimentally, in the following manner:

We imagine, in the direction of length of a cylindrical tube of the section q, a small separated distance dx. It encloses a small cylindrical volume that contains the amount of the substance equal to $\mu q dx$, where q is the specific gravity of the constituent of the

solution (or the substance). This amount will remaint immovable as long as the chemical intensity Π of the substance, in the sections immediately touching this section, is not different from *its* chemical intensity. The difference of intensity in the distance dx, is therefore to be looked upon as the cause of the motion of the constituent, and we assume that *the velocity u of the motion in the direction x is proportional to the difference of intensity in this direction :*

$$u = -h\frac{\partial \Pi}{\partial x} \tag{1}$$

The proportional factor h might be called the activity * of the constituent. Its unit is sec, for the unit of Π is $cm^2 : sec^2$. Since by page 123, eq. (21), by constant pressure and temperature θ,

$$\Pi = A + R\theta lC, \tag{2}$$

where A is a constant, C the concentration of the constituent, and R its specific gas constant. We obtain therefore

$$C \,.\, u \,.\, = -hR\theta \frac{\partial C}{\partial x}. \tag{3}$$

If n mols of the salt are dissolved in n_0 mols of the solvent, then, when C_0 is the concentration of the solvent,

$$C = \frac{n}{n_0 + n}, \qquad C_0 = \frac{n_0}{n_0 + n}; \tag{4}$$

$$\frac{\partial C}{\partial x} = \frac{n_0}{(n_0 + n)^2} \cdot \frac{\partial n}{\partial x} = \frac{C_0}{n_0 + n}\frac{\partial n}{\partial x}.$$

* Beweglichkeit.

If we use instead of the number of mols n, the specific gravity, μ, of the salt, i.e., the number of grams in cc. ($\because \mu = n \,.\, m$, where n is referred to cc. and m is the molecular weight), it follows from (3)

$$\mu u = - hR\theta C_0 \frac{\partial u}{\partial x} = - K \frac{\partial \mu}{\partial x}. \tag{5}$$

Here the left side, μu, is the amount of the constituent which wanders in the time 1, through the section 1 in the direction x. It is proportional to the difference of density of the constituent in this direction (or to the differential quotients of the density taken in the opposite direction).

The entrance of the constituent through the one, and its exit through the other section of the volume considered, of the length x increases, as is self-evident, the amount of substance in each cubic centimeter between the two sections in the time 1, by the amount

$$\frac{\partial \mu}{dt} = - \frac{\partial (\mu u)}{\partial x} = K \frac{\partial^2 \mu}{\partial x^2}. \tag{6}$$

The hypothesis (1) that has thus led us to the law of diffusion is in complete accord with the formulæ for the diffusion of other forms of energy. If instead of the chemical intensity we substitute the temperature, the pressure, or the electrical potential, we obtain the well-known and proven laws for the forms of energy.

The diffusion constant k of eqs. (5) and (6) has the value

$$k = h \,.\, R\theta \,.\, C_0, \tag{7}$$

and for highly diluted solutions

$$k = h \,.\, R\theta. \tag{7b}$$

Its unit is found from that as from other formulæ to be cm.^{2} : sec. Experience shows that h, for different substances, is different, and also has a value depending upon the temperature, and Nernst has succeeded in bringing the value of h for electrolytes, in a form consistent with the theory. When we remove from his calculations * the molecular starting-point, it is essentially as follows:

We assume, with Arrhenius, that each electrolyte is formed of two constituents, equally mixed, which change their positions by electrolysis; we therefore have two intensities, Π_A and Π_K, instead of Π, so that in the energy equation, instead of ΠdM, we have the sum $\Pi_A dM_A + \Pi_K dM_K$. Since, however, the changes of mass dM, dM_A, and dM_K of the electrolytes depend upon the electrochemical equivalents α, α_1, α_2 of these substances, we have

$$\Pi\alpha = \Pi_A\alpha_1 + \Pi_K\alpha_2. \tag{8}$$

Nernst's theory considers now the diffusion of electrolytes, as the diffusion of these two constituents. If h_1 and h_2 are the "activities" (Beweglichkeiten) of the ions, then the velocity of their motions, as in the case of ordinary diffusion, will be

$$u = -h_1\frac{\partial \Pi_A}{\partial x}, \quad u = -h_2\frac{\partial \Pi_K}{\partial x}. \tag{9}$$

* Nernst, Theoretical Chemistry, trans. by Palmer, Ger. ed. p. 309 and fol.

If these equations are multiplied by $\alpha_1 h_2$ and $\alpha_2 h_1$ respectively, and added, it follows, by aid of (8), that

$$u = -\frac{\frac{h_1}{\alpha_1}\cdot\frac{h_2}{\alpha_2}}{\frac{h_1}{\alpha_1}+\frac{h_2}{\alpha_2}}\alpha\cdot\frac{\partial \Pi}{\partial s}. \tag{10}$$

The comparison of (1) with (7*b*) gives the diffusion constant for high dilution as

$$k = \frac{\frac{h_1}{\alpha_1}\cdot\frac{h_2}{\alpha_2}}{\frac{h_1}{\alpha_1}+\frac{h_2}{\alpha_2}}\alpha R\theta. \tag{11}$$

Upon the "activities" h_1 and h_2, however, the electrolytic phenomena depend.

In electrolysis the velocities u_1 and u_2 of the ions are no longer equal, as with the ordinary diffusion of electrolytes. It is not in consequence of a difference in concentration, but in consequence of a difference of the electrical potential P, that now the chemical intensity of each ion varies from place to place, and causes motion. If the ordinary diffusion does not take place at the same time as that by electrolysis, then the intensities differ only in consequence of the potential P, and are functions of this potential alone.

Equation (1) gives, therefore, of ion velocities

$$\left\{\begin{aligned} u_1 &= -h_1\frac{\partial \Pi_A}{\partial x} = -h_1\frac{\partial \Pi_A}{\partial P}\cdot\frac{\partial P}{\partial x}, \\ u_2 &= -h_2\frac{\partial \Pi_K}{\partial x} = -h_2\frac{\partial \Pi_K}{\partial P}\cdot\frac{\partial P}{\partial x}. \end{aligned}\right. \tag{12}$$

In order now to find the differential quotients of the intensity, according to the electrical potential, we follow the same method as we used on page 124 for the corresponding case. We start from the energy equation (12), page 107,

$$(13) \qquad dE = \theta dS - Pd\epsilon + \Pi_A dM_A + \Pi_K dM_K,$$

in which dE is the energy passing through the section in the unit of time, $d\epsilon$ the amount of electricity, dM_A and dM_K the amounts of the anion and kathion going through, dS the entropy, and θ the temperature. We write

$$(14) \quad d(E + P\epsilon) = \theta dS + \epsilon dP + \Pi_A dM_A + \Pi_K dM_K,$$

and conclude from the property of a complete differential that

$$(15) \qquad \frac{\partial \Pi_A}{\partial P} = \frac{\partial \epsilon}{\partial M_A}, \quad \frac{\partial \Pi_K}{\partial P} = \frac{\partial \epsilon}{\partial M_K}.$$

Now the amount of electricity is, according to page 101, bound to the ions, and just as much on the anion as on the kathion, and on each equivalent of the electrolyte the amount $x\epsilon = \frac{\epsilon}{\epsilon_0}$, where $x = \frac{1}{\epsilon_0} = 1.036 \cdot 10^{-14}$, and ϵ is measured in absolute units. We have

$$(16) \qquad \frac{d\epsilon}{\epsilon_0} = \frac{dM_A}{2\alpha_1} + \frac{dM_K}{2\alpha_2}$$

and from equation (12) and (15)

$$(17)\quad u_1 = -h_1 \frac{1}{2x\alpha_1} \cdot \frac{\partial P}{\partial x}, \quad u_2 = -h_2 \frac{1}{2x\alpha_2} \cdot \frac{\partial P}{\partial x}.$$

On the other hand, it follows from equation (18) page

$$(18)\qquad u_1 = -x\mu_1 \cdot \frac{\partial P}{\partial x}, \quad u_2 = -x\mu_2 \frac{\partial P}{\partial x}.$$

where μ_1 and μ_2 are the molecular conductivities of the ions. The comparison gives

$$(19)\qquad \frac{h_1}{x\alpha_1} = 2x\mu_1, \quad \frac{h_2}{x\alpha_2} = 2x\mu_2;$$

or according to page 108, by using the conductivities observed by Kohlrausch and the degree of dissociation η,

$$(19b)\ \frac{h_1}{x\alpha_1} = 2\mu_1^* \cdot x \cdot \sigma_{Hg} \cdot \frac{1000}{\eta}, \quad \frac{h_2}{x\alpha_2} = 2\mu_2^* \cdot x \cdot \sigma_{Hg} \cdot \frac{1000}{\eta}.$$

By using these results we obtain

$$\frac{h_1}{x\alpha_1} = 2\mu_1^* \cdot 1.036 \cdot 10^{-4} \cdot 1.063 \cdot 10^{-5} \cdot \frac{1000}{\eta};$$

$$(19c)\ \frac{h_1}{x\alpha_1} = 2\mu_1^* \cdot 1.10 \cdot 10^{-6} \frac{1}{\eta}, \quad \frac{h_2}{x\alpha_2} = 2\mu_2^* \cdot 1.10 \cdot 10^{-6} \frac{1}{\eta},$$

If the electrolyte is completely dissociated into ions, i.e., $\eta = 1$, it follows

$$(20)\quad \frac{h_1}{x\alpha_1} = 2\mu_1^* \cdot 1.10 \cdot 10^{-6}, \quad \frac{h_2}{x\alpha_2} = 2\mu_2^* \cdot 1.10 \cdot 10^{-6}.$$

If we write now by page 27

$$(21)\qquad R_0\theta = \frac{2.270}{273} \cdot 10^{10} \cdot \theta,$$

then for univalent substances, by which the mol and equivalent are the same,

$$\alpha R\theta = 2.270\,\frac{\theta}{273} \cdot 10^{10};$$

and it follows from (11)

$$(22)\quad k = \frac{\mu_1^*\mu_2^*}{\mu_1^* + \mu_2^*} \cdot 2 \cdot 1.10 \cdot 10^{-6} \cdot 1.036 \cdot 10^{-4} \cdot 2.270 \cdot 10^{10} \cdot \frac{\theta}{273}.$$

Since the value of μ^* for 18° C. has been observed, it is better to use $\theta = 273 + \vartheta = 291 + (\vartheta - 18)$; hence

$$k = \frac{\mu_1^*\mu_2^*}{\mu_1^* + \mu_2^*}\, 2 \cdot 1.10 \cdot 1.036 \cdot 2.270 \cdot \frac{291}{273}\left[1 + \frac{\vartheta - 18}{291}\right];$$

$$(23)\quad k = 5.525 \cdot \frac{\mu_1^*\mu_2^*}{\mu_1^* + \mu_2^*} \cdot [1 + 0.0034(\vartheta - 18)]\frac{\text{cm.}^2}{\text{sec.}}.$$

The cm.^{2} : sec. is transformed into cm.^{2} : days by multiplication by $8.64 \cdot 10^4$.

$$(23b)\quad k = 0.477 \cdot 10^6 \cdot \frac{\mu_1^*\mu_2^*}{\mu_1^* + \mu_2^*} \cdot [1 + 0.0034(\vartheta - 18)]\,\frac{\text{cm.}^2}{\text{day}}.$$

If we choose, for example, with Nernst the values 4.2 and 6.3 (18°) for Na ($\mu_1^* 10^6$) and Cl ($\mu_2^* 10^6$), it

follows for NaCl that $k = 1.20$, while Scheffer's observation gave 1.11.

The increasing of the molecular conductivity by about 2 per cent for each degree of temperature leads to an increase of k of 0.023 $\times$ its value for each degree, which agrees very well with the observation.

CHAPTER VII.

THE VELOCITY OF A CHEMICAL REACTION.

THE assumption that the velocity of diffusion, u, is proportional to the difference of chemical intensity,

$$u = -h \frac{\partial \Pi}{\partial x},$$

allows us deeper insight into the subject. We can assume that, in analogy to the behavior of the intensities of other forms of energy, each chemical intensity strives to expand. If there are, in the two sections that bound, at the distance x, a cylindrical volume, two chemical intensities Π_1 and Π_2, then, according to this view, the diffusion in this volume is caused by the two different forces, each striving to expand its own chemical state; and the stronger must succeed. By this we introduce no new method of consideration; but only apply to chemical phenomena the ordinary representation of the process of diffusion.

In chemical processes we find but one objection to this, that is, that though the expansion may be one of position, as in diffusion, it is not compulsory that it

should be so. In the case of the inversion of sugar, for example, the chemical reaction takes place regularly and uniformly in all parts, and as the time increases the number of mols inverted also increases. If N is the number of mols that are present at the chemical intensity Π, then

$$\frac{dN}{dt} = k\Pi, \tag{1}$$

where k is a constant proportional factor. That is, *the increase in the number of mols which enter into reaction in the time dt is proportional to the intensity.* According to pages 133 and 134 the intensity of a reaction is composed of the intensities of its reacting constituents, and if we measure the progress of the reaction by the change, in unit time, of the number of mols N_0 of any of the changing constituents, as, for example, one which decreases by the reaction, it follows for constant pressure and temperature, by aid of eq. (21), page 125,

$$-\frac{dN_0}{dt} = k_0 R_0 \theta l\left(C_1^{\nu_1} C_2^{\nu_2} \ldots C_n^{\nu_n}\right) + \Phi_0. \tag{2}$$

Here Φ_0 is a quantity dependent only upon the pressure and temperature. C is the concentration, ν the exchange numbers of the n reacting constituents, θ the absolute temperature, R_0 the general gas constant, k_0 a constant whose value depends, among other things, upon the choice of the constituents, according to the molecular weight, N_0, by which the progress of the reaction is measured.

After entrance of equilibrium the concentration product has become k_0, a value depending upon pressure and temperature. It is

$$o = k_0 R_0 \theta l K_0 + \Phi_0;$$

and, by subtracting this from the former we eliminate Φ, and obtain

$$(3) \qquad -\frac{dN_0}{dt} = k_0 R_0 \theta l \frac{1}{K_0} C_1^{\nu_1} C_2^{\nu_2} \ldots C_n^{\nu_n}.$$

If now we designate those constituents which have positive exchange numbers (i.e., those that increase during the reaction) by the indices a, b, c . . ., and the decreasing ones with α, β, γ . . ., it follows

$$(4) \quad -\frac{dN_0}{dt} = k_0 R_0 \theta \{ l C_a^{\nu_a} C_b^{\nu_b} \ldots - l K_0 C_\alpha^{\nu_\alpha} C_\beta^{\nu_\beta} \ldots \}.$$

We will only follow the subject further under the condition that the two concentration products,

$$c = C_a^{\nu_a} C_b^{\nu_b} \ldots, \quad \eta = K_0 C_\alpha^{\nu_\alpha} C^{\beta\nu_\beta} \ldots,$$

differ but slightly from one another, i.e., that the reaction goes very slowly, a condition that must be fulfilled anyway on account of the constant temperature. In this case

$$l\frac{c}{\eta} = 2\frac{\frac{c}{\eta} - 1}{\frac{c}{\eta} + 1} = 2\frac{c - \eta}{c + \eta},$$

and since $\frac{c+\gamma}{2}$ changes but slightly during the reaction, and by neglecting the small quantities, of a higher order than $c - \gamma'$, we can write

$$(5) \qquad -\frac{dN_0}{dt} = \frac{2k_0R_0\theta}{c+\eta}(c-\eta) = M_0C_a^{\nu_a}C_b^{\nu_b}\ldots - \mathbf{M}_0C_\alpha^{\nu_\alpha}C_\beta^{\nu_\beta}\ldots,$$

where M_0 and $\mathbf{M}_0 = K_0M_0$ are constants.

Finally, we introduce the same term as we did on page 142. We will measure the amounts of the constituents that were present at first, and which increase, in equivalents and call them $A, B\ldots$, their exchange numbers are a, b; the equivalents present at first of the decreasing substances are then $\mathbf{A}, \mathbf{B}\ldots$, and their exchange numbers $\alpha, \beta, \gamma\ldots$; and, finally, we will designate by x the proportional number of equivalents, n_0, which have reacted during the time t seconds. Then

$$(6) \quad \frac{dx}{dt} = -M(A+x)^a(B+x)^b\ldots + \mathbf{M}(\mathbf{A}+x)^\alpha(\mathbf{B}-x)^\beta\ldots,$$

where M and $\mathbf{M}$ are new constants, and $\mathbf{M} = MK$, when K depends only upon pressure and temperature, and condition the entrance of equilibrium (page 143).

If x equivalents are transformed, then

$$K = (A+x)^a(B+x)^b\ldots \div (\mathbf{A}-x)^\alpha(\mathbf{B}-x)^\beta\ldots.$$

The law according to which a slow reaction takes place is, under all circumstances, expressed by the inte-

gral of a rational function, i.e., by logarithms and rational functions. The law of Guldberg and Waage, page 143, is a special form of eq. (6). At $dx : dt = 0$ the kinetic process becomes a static one.

If a reaction takes place in one direction only, so that equilibrium is reached only after the constituents, which decrease by the reaction, are all used up, so that $K = \infty$, i.e., M negligibly small as compared to **M**, then the equation is

$$\frac{dx}{dt} = -M(\mathbf{A} + x)^a(B + x)^b + N, \tag{7}$$

or

$$\frac{dx}{dt} = M.(A - x)^\alpha(B - x)^\beta. \tag{7b}$$

The first is for a finite value of M, and the latter for very small M: in the first case **M** is so large that the change in the value of x is without influence upon the second term; this therefore retains a constant value N.

The oldest confirmation of the theory are the results of the experiments of Wilhelmy, 1850, on the inversion of raw sugar. In a water solution this falls into Dextrose and Levulose, according to the formula

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6.$$

Since a state of equilibrium is only reached here after complete disappearance of the sugar, eq. (7b) must be used. Neglecting the concentration of the water, we find

$$\frac{dx}{dt} = \mathbf{M} \cdot (A - x), \tag{8}$$

where A is the initial amount of sugar in the solution, and x the amount inverted in the time t.

It is not necessary here to measure these amounts by equivalents, for there is but one substance present, and we can measure it as well by grains or any other unit. By integration we find

$$A - x = Ae^{-Mt}, \quad l\frac{A - x}{A} = -\mathbf{M} \cdot t.$$

In order to measure the amount of sugar inverted Wilhelmy used the polariscope. Since the angle through which the analyzer is turned is proportional to the amount of sugar, these angles can be used instead of the weight or equivalents. He found, for example, after lapse of

0	15	60	105	120	∞ minutes

the angle was

46°.75	43°.75	35°.75	28°.25	26°.0	−18°.70

We have then

$A - x =$	65.45	62.45	54.45	46.95	44.70	0
$^{10}\log \frac{A}{A - x} =$	0	0.02038	0.07991	0.14427	0.16560	∞
$\frac{1}{t} {}^{10}\log \frac{A}{A - x} =$		0.00136	0.00133	0.00138	0.00138	

from which the truth of the law can be seen.

Ostwald has measured the accelerating action of an acid (catalytic action) upon the decomposition of an

ester in a water solution, by titration. He adds, for example, to 1 c.c. methyl acetate 10 c.c. HCl (1 mol in liter), dilutes with water to 15 c.c. and titrates a sample after

0 14 34 199 539 ∞ minutes

with dilute barium hydroxide solution. At first

13.33 c.c.

of $Ba(OH)_2$ were needed to neutralize the free acid, but during the catalysis the amount of acetic acid formed, made it necessary to add

0.92 2.14 8.82 13.09 14.11 c.c.

more than at first. The amount of ester originally present is represented by 14.11, and we find of $A - x$

14.11 13.19 11.97 5.29 1.02 0

and by use of logarithms

$\log \frac{A}{A-x}$	= 0.0293	0.0714	0.4261	1.1409	0
$\frac{1}{t} \log \frac{A}{A-x}$	= 0.00209	0.00210	0.00214	0.00212	

so that the value which should be constant, according to the theory, is so within the experimental error.

The saponification of an ester is an example of a reaction, by which *two* substances change their concentration, and leads to a complete reaction, i.e., one to

which equation (7*b*) applies. According to the formula

$$\underset{\text{Ethyl acetate}}{C_2H_5COOCH_3} + \underset{\text{Caustic soda}}{NaOH} = \underset{\text{Sodium acetate}}{CH_3COONa} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}.$$

the ester changes place in water solution with the base. The amount, changed, in mols, for the time t can be determined by titration of the base, and if A and B are the number of mols of ester and base originally present, then

$$\frac{dx}{dt} = (\mathbf{M}A - x)(B - x)$$

by transforming it into

$$\frac{dx}{B - A}\left(\frac{1}{A - x} - \frac{1}{B - x}\right) = -\mathbf{M}dt,$$

it is apparent that the integral of the differential equation, which has $t = 0$ when $x = 0$, is

$$\frac{1}{B - A} l\frac{B - x}{A - x}\frac{A}{B} = \mathbf{M}t.$$

If at first the base and ester are present in equivalent amounts, i.e., $A = B$, then the differential equation is simplified to

$$\frac{dx}{dt} = \mathbf{M}(A - x)^2,$$

and its integral is

$$\frac{x}{A(A - x)} = \mathbf{M}t.$$

Nernst gives the following series of observations to illustrate the equation which holds for $A \gtrless B$.

The reaction as given above, at 10°, after

$t =$ 0 4.89 10.37 28.18 ∞ minutes,

when 100 cc. was titrated with $\frac{1}{23.26}$ normal acid, gave

$T =$ 61.95 50.59 42.40 29.35 14.92 cc.

The division of these numbers by 23.26 give the number of mols in a liter, of the base, still present, i.e. $B - x$. The value for $t = \infty$ gives $B - A$. We obtain, therefore, by logarithms

$$M = \frac{2.303 \times 23.26}{14.92t} \cdot {}^{10}\log \frac{47.03}{61.95} \cdot \frac{T}{T - 14.92},$$

which gives

0.0236 0.0238 0.0233

As an example of the general equation (6) the formation of an ester can serve very well. The mixture of 1 mol of alcohol with 1 mol of acetic acid causes the formation of ethyl acetate according to the formula

$$CH_3COOH + C_2H_5OH = CH_3COOC_2H_5 + H_2O.$$

The number of mols, x, used during the time t must, where none of the final product was present at first, satisfy the equation

$$\frac{dx}{dt} = \mathbf{M}(1 - x)^2 - Mx^2,$$

the integral of which (for $t = 0$, $x = 0$) is

$$(a - b)(\mathbf{M} - M)t = \log \frac{x - a}{x - b} \cdot \frac{b}{a},$$

where a and b are the roots of the equation

$$x^2 = 2\frac{\mathrm{M}}{\mathrm{M} - M}x + \frac{\mathrm{M}}{\mathrm{M} - M} = 0.$$

Since in the case considered equilibrium is attained after decomposition of 2/3 of a mol, i.e., $\frac{dx}{dt} = 0$ for $x = 2/3$, it follows

$$\frac{\mathrm{M}}{M} = 4, \quad a = 2, \quad b = 2/3;$$

$$\frac{4}{3}(\mathrm{M} - M) = \frac{1}{t}\log\frac{2 - x}{2 - 3x}.$$

Guldberg and Waage have proven this formula and found only a fair agreement with the theory, which would have been much better if x, for the completed reaction, had not been taken as exactly 2/3, but had been determined each time by observation.

Further examples can be found in the works of Ostwald and Nernst, which have been mentioned previously.

PART IV.

THE DEGREES OF FREEDOM OF CHEMICAL PHENOMENA.

CHAPTER I.

THE RULE OF PHASES.

By the equation

$$dE \leqq \theta dS - PdV + \Pi_1 dM_1 + \Pi_2 dM_2 + \ldots + \Pi_n dM_n,$$

which holds for any homogeneous body, each possible change is made dependent on those changes which are necessary to its definition. The state of a body is determined when, besides the n amounts of substance M_1, $M_2 \ldots M_n$ (which are independent of one another), the temperature θ and pressure P are known, provided that besides changes of substance only changes in heat and volume take place, and especially that those in electricity, gravity, and surface energy are excluded. The $n+2$ variables can occur in the same manner in the energy equation by writing it as follows:

$$d(E - \theta S + PV) \leqq Sd\theta - VdP + \Pi_1 dM_1 + \Pi_2 dM_2 + \ldots + \Pi_n dM_n.$$

Here all the terms on the left, S, V, Π_1, Π_2, ... Π_n, are functions of θ, P, M, $M_2 \ldots M_n$.

If we ask what possible changes a certain amount, say 1 gram, of the homogeneous body is capable of undergoing, the answer is $n + 1$, since by condition $M_1 + M_2 + \ldots + M_n = 1$ gr. In this way the possible states of a gram of water has a freedom of two dimensions; only pressure and temperature can vary. On the other hand, 1 gram of a mixture of oxygen and hydrogen can vary in three ways—in temperature, pressure, and composition.

The case is slightly different when two phases, which contain the same n substances independently variable, form a system between which exchange of substance is possible. We have from page 115

$$dE' \leqq \theta' dS' - P' dV' + \Pi_1' dM_1' + \Pi_2' dM_2' + \ldots \Pi_n' dM_n';$$
$$dE'' \leqq \theta'' dS'' - P'' dV'' + \Pi_1'' dM_1'' + \Pi_2'' dM_2'' + \ldots \Pi_n'' dM_n'';$$

that is, $2(n + 2)$ variables, viz., θ', P', M_1', $M_2' \ldots M_n'$, and θ'', P'', M_1'', $M_2'' \ldots M_n''$. We know, however, that between them, in the case of equilibrium, there are $n + 2$ conditions.

$$\theta' = \theta'', \quad P' = P'', \quad \Pi_1' = \Pi_1'', \quad \Pi_2' = \Pi_2'', \ldots \Pi_n' = \Pi_n''.$$

In case of equilibrium the mass of each phase is a fraction of the total mass, dependent on the temperature, pressure, and composition. This may be looked upon here as an *experimental law*, which, however, we

will prove from our theoretical standpoint in the next chapter. If the total mass amounts to 1 gram, then the expressions $M_1' + M_2' + \ldots + M_n'$ and $M_1'' + M_2'' + \ldots + M_n''$ must be certain functions of the other variables. As independent variables we can take the above $2(n+2)$ quantities only so long as all, even those which cancel at the equilibrium of the two phases, are considered. When the still possible changes are not to disturb the equilibrium, there would remain only

$$2(n+2) - (n+2) - 2 = n$$

variables. For example, the states of a gram of fluid, as well as one of gaseous, water can be changed each in two ways. If the two phases are brought together, then to the four variables a fifth is added, viz., the exchange of substance from one state to the other. These two grams of water do not, however, in general remain in equilibrium. If after entrance of a state of equilibrium it is to be retained during changes, then the three conditions necessary are equality of pressure, temperature, and chemical intensity in the two phases; and a fourth is given from the fact that the pressure is a function of the temperature, by the law of vapor tension, and consequently the composition of the two phases is determined. The mixture has therefore but *one degree* of freedom; if *one* of the variables is known as the temperature, then we know all the others.

We can, from the simple case given as an example, also show it geometrically, when in addition to pressure and temperature we use the chemical intensity of

1 gram of water as a coördinate. For one gram of fluid water and one in the gaseous state we obtain two different surfaces in the pressure-temperature plane. The two intersect in a curve, i.e., where the pressure and temperature is given, by which liquid and gaseous water can exist together, and by which the two phases can exchange; the states in which this is possible form a system of *one* dimension. For the general case of a freedom of more than two dimensions we can do nothing geometrically.

For r phases, finally, by which there are $r(n+2)$ variables, since in each two phases the temperatures, pressures, and intensities must be equal, we find $(r-1)(n+2)$ conditions, and by the fact that the mass of each phase is a *certain* fraction of the total mass, depending upon the temperature, pressure, etc., we find still r conditions. We have therefore remaining

$$r(n+2)-(r-1)(n+2)-r=n+2-r$$

independently varying quantities. Therefore, when n substances are present in r different phases, and enter into exchange of substance, the equilibrium remains by $n+2-r$ different kinds of possible changes, or *the equilibrium of substances in r phases is a state of* $n+2-r$ *dimensions.*

This law, discovered by Gibbs, is not changed when in a single phase less than n substances are present. We can in all phases imagine the maximum of n substances and assume the terms dM partly equal to zero (without retaining them).

In the pressure-temperature plane we can also represent in general the proportions, as far as concerns changes of 1 and 2 dimensions. If only one substance is present it must be in 2 phases, 2 substances must be in 3 phases, and n substances must be present in $n + 1$ phases, if the equilibrium is to be changed unidimensionally, and when to each pressure the temperature is to be determined or a curve in the pressure-temperature plane is to represent the possible states. If we have represented in this plane the curves of unidimensional (*so-called complete*) states of equilibrium, then between them lie those states by which pressure and temperature can be chosen independently of one another, i.e., by presence of n substances, in at most n phases, in a state of exchange. How the phases present are to be divided among the n single fields of the plane is given in part by the condition that in each division line of a field $n + 1$ phases, and in each intersecting point of the boundary line $n + 2$ phases must come together, the latter because by the point each possibility of change is excluded, or occurs in a state of zero dimensions.

One glance at Fig. 5, page 87, for the possible states of a single substance will make all clear.

The cases in which 2 substances form a number of phases have been investigated by Roozeboom. Sulphurous acid and water form the following phases: *I*, ice; *H*, solid hydrate, $SO_2 + 7H_2O$; *S*, liquid acid with small amounts of water; *h*, water solution of sulphurous acid; and finally a gas *G*, composed of water vapor and gaseous sulphurous acid. Two liquid phases

must be different, because water and liquid SO_2 exist together somewhat as ether and water, and like these substances dissolve one another slightly. The 5 phases cannot exist together in equilibrium; each four exist in the single points, of which Roozeboom has investigated 2, each 3 in curves that go from the points, and each 2 in the fields between. So much as has been studied is shown in Fig. 14.

The fourfold point B, at which the phases I, H, L, and G coexist, has the coördinates $\vartheta = -2°.6$, $p = 21.1$ cm.; and the fourfold point C, by which H, L, S,

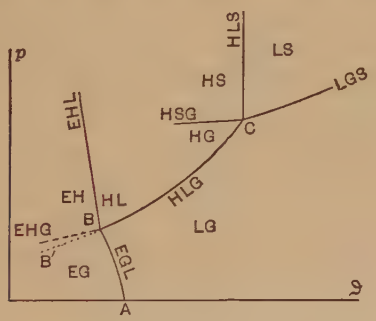


FIG. 14.

and G coexist has $\vartheta = 12°.1$, $p = 177$ cm. AB gives the relation between pressure and temperature that must be held in order that a water solution of sulphurous acid, in which there is ice, is in equilibrium with its vapor.

The strength of acid in the water becomes smaller as the pressure becomes less, that in the vapor becomes larger, so that the curve A nears the melting-point of ice. The curve BC is the curve of vapor tension of a

water solution of sulphurous acid which is in contact with solid hydrate, i.e., the curve of vapor tension of the concentrated solution; the dotted continuation BB' is the non-reversible change of state, the so-called overcooled state.

In this way the figure can be understood by the initials of the different states. How HL, HS, and HG are transformed into one another, was not investigated, it is plainly a state of the system which is not determined by pressure and temperature, and so the mixing proportions of H_2O and SO_2 must be taken as a third variable. We would find there states in which, by a given pressure temperature, two different pairs of phases could exist; as well as those in which pairs of phases could not exist, they consist of the single substances separated from one another.

CHAPTER II.

THE EQUILIBRIUM OF PHASES.

On page 203 we used a law as an experimental one; we will now derive it theoretically in the way that its discoverer, Gibbs, did. The possible changes which a part M' of a single phase in a system can undergo must satisfy the equation

$$(1) \qquad dE' \leqq \theta dS' - PdV' + \Pi_1 dM' + \Pi_2 dM_2' + \ldots \Pi_n dM_n',$$

where

$$M_1' + M_2' + \ldots + M_n' = M'.$$

The equation can be transformed into

$$(2) \quad -d\{E' - \theta S' + PV' - \Pi_1 M_1' - \Pi_2 M_2' - \ldots - \Pi_n M_n'\} \geqq S'd\theta - V'dP + M_1'd\Pi_1 + M_2'd\Pi_2 + \ldots + M_n'dM_n,$$

always under the condition that

$$M_1' + M_2' + \ldots + M_n' = M'.$$

Since now by transposition from one phase to another the differentials on the right are all 0, the function

$$(3a)\quad F = E' - \theta S' + PV' - \Pi_1 M_1' - \Pi_2 M_2' + \ldots \Pi_n M_n'$$

(which is called the thermodynamical potential or the free energy at constant pressure, temperature, and chemical intensity) has the same value as

$$(3b)\quad F'' = E'' - \theta S'' + PV'' - \Pi_1 M_1'' - \Pi_2 M_2'' - \ldots \Pi_n M_n'',$$

as has each *corresponding* function of this form to every other phase, *provided* that the transformation is reversible and the condition holds that

$$M' = M'' = \ldots$$

On this ground we can answer the question, as to how reversible changes of pressure, temperature, and intensity must be composed in order that the possibility of coexistence of each phase remains. The functions $F', F'' \ldots$ must have the same value, and when this common function is represented by F the equation must hold that

$$(4)\quad \begin{aligned} dF = dE' &- \theta dS' + PdV - \Pi_1 d M_1' - \Pi_2 d M_2' \\ &- \ldots \Pi_n d M_n' - S' d\theta + V' dP - M_1' d\Pi_1 \\ &- M_2' d\Pi_2 - \ldots M_n' d\Pi_n' ; \end{aligned}$$

that is, by (1),

$$(5)\quad \begin{aligned} dF = &- S' d\theta + V' dP - M_1' d\Pi_1 - M_2' d\Pi_2 \\ &- \ldots - M_n' d\Pi_n , \end{aligned}$$

where

$$M_1' + M_2' + \ldots + M_n = M'.$$

There are as many relations in the form (5) as there are phases which exist beside one another,—let us say r. The elimination of F gives us therefore $r - 1$ relations between the differentials $d\theta$, dP, $d\Pi_1$, $d\Pi_2$, $\ldots$ $d\Pi_n$, which must be fulfilled if these changes are not to disturb the equilibrium between the phases.

Together with the constants of the total mass, there are also r conditions which determine the mass of each of the r phases, as in the previous chapter we found to be a result of experiment.

If only one substance is present in two phases, then

$$\begin{aligned} dF &= -S\,d\theta + V'dP - M'd\Pi \\ &= -S''d\theta + V''dP - M''d\Pi \\ M' &= M'' \\ M_1' &= M_2''; \end{aligned}$$

therefore

$$(6) \qquad (S'' - S')d\theta = (V'' - V')dP,$$

an equation that leads to relation (7), page 81.

For two substances in two phases we have the equations

$$\begin{aligned} dF &= -S'd\theta + V'dP - M_1'd\Pi_1 - M_2'd\Pi_2 \\ &= -S''d\theta + V''dP - M_1''d\Pi_1 - M_2''d\Pi_2 \\ M_1' + M_2' &= M_1'' + M_2'', \end{aligned}$$

and they give

$$(7) \quad (S'' - S')d\theta = (V'' - V')dP - (M_1'' - M_1')d(\Pi_1 - \Pi_2).$$

If $M_1'' = M_1'$, then $M_2'' = M_2'$; i.e., if both phases have the same ratio of mixture, then the equation is the

same as for a single substance. If this ratio is different, then beside the given four possible changes, $d\theta$, dP, $d\Pi_1$, $d\Pi_2$, the relation exists that the amount of the mixture open to change remains constant, as for example 1 gram. It will therefore be possible to make all dependent upon the two variables θ and P. The above equation can therefore be written

$$(8)\quad \left[S'' - S' + (M_1'' - M_1')\frac{\partial(\Pi_1 - \Pi_2)}{\partial\theta}\right]d\theta = \left[V'' - V' - (M_1'' - M_1')\frac{\partial(\Pi_1 - \Pi_2)}{\partial P}\right]dP.$$

If, by a certain ratio of mixture, the factor of dP on the right becomes 0, therefore $\frac{d\theta}{dP} = 0$, the curve of vapor tension has a tangent parallel to the axis of pressure, a case to which Duhem refers certain phenomena that are shown by the liquefaction of mixtures of gases.

Instead of pressure and temperature, we can also use pressure and ratio of mixture as independent variables, where the latter is given by M_1'. We obtain

$$(8b)\quad (S'' - S')\left(\frac{\partial\theta}{\partial P}dP + \frac{\partial\theta}{\partial M_1'}dM_1'\right) = (V'' - V')dP - (M_1'' - M_1')\left[\frac{\partial(\Pi_1 - \Pi_2)}{\partial P}dP + \frac{\partial(\Pi_1 - \Pi_2)}{\partial M_1'}dM_1'\right].$$

At constant pressure $dP = 0$, $\frac{\partial\theta}{\partial M_1'} = 0$, if $M_1'' = M_1'$; i.e., the temperature at constant pressure

is a maximum or minimum for the case that both phases show the same ratio of mixture (Gibbs).

In a corresponding manner we can prove by introduction of θ and M_1' as independent variables that by all mixtures, at the same temperature, the one in which both phases have the same ratio, shows the greatest or the smallest pressure.

CHAPTER III.

CHEMICAL REACTIONS THAT DEPEND UPON SEVERAL PARAMETERS.

THE basis of all calculations in chemistry is the measuring of the amounts of the reacting substance according to the different units; each chemically different substance has a different amount for its mass which is called a mol, and is used together with its fractions, the atomic and equivalent weights. The mass occurs in all our energetic equations in the form that its differential is multiplied into the chemical intensity; that is, as a quantity or capacity function (see page 43) of chemical energy.

Chemistry, from a mathematical standpoint, has up to the last ten years done nothing but work out the measurement of amounts of substance. By the development of the idea of molecular weight it has succeeded in representing the majority of chemical processes as a function of one independent parameter, i.e., it has found how to measure the amounts, so that when we know the change that an amount of substance undergoes by a process we can give that for all the other reacting substances. We have united in this way, in our equations of simple chemical reactions, the terms of chemical energy to a single term of the form $\Pi_0 dM_0$.

As the later mathematical development of chemistry has turned all its attention to the intensity factor Π and taken for granted that the quantity factor M is well known, so have we, in our explanations, busied ourselves but little with stoichiometry. For example, we have had no chance to study the hypotheses of the molecular constitution of matter, which has only retained its place for the ease by which it allows us to review the relations of mass.

It will be well, therefore, in concluding, to investigate *stoichiometry*, that oldest branch of mathematical chemistry which concerns those processes which do not depend upon a single parameter.

The reactions

$$\begin{aligned} H + Cl &= HCl, \\ 2H + O &= H_2O \end{aligned}$$

are two processes, each of which depends upon a single parameter.

If we measure each of the occurring substances in mols, and if in a very small period of time H reacts with x, Cl with y, and O with z atoms, HCl with u and H_2O with v mols, then it is necessary that

$$(1) \qquad x = y = u, \quad \frac{x}{2} = z = v;$$

hence the proportions of the reacting substances are determined, and only *one* of the number is necessary to find the others.

If, however, we have a mixture of H, Cl, and O, there remains, even when we are certain that only the above reactions take place, an uncertainty. The amount

of hydrogen falls now into two parts, in x_1 and x_2 mols, so that

$$(2) \qquad x = x_1 + x_2, \quad x_1 = y = u, \quad x_2 = 2z = 2v$$

when the reaction goes smoothly, i.e., when no Cl, H, or O remains over. It also follows from

$$(3) \qquad x \,.\, \mathrm{H} + y \,.\, \mathrm{Cl} + z \,.\, \mathrm{O} = u\mathrm{HCl} + v \,.\, \mathrm{H_2O},$$

by the law of the conservation of matter, that

$$(4) \qquad x_2 = u + 2v, \quad y = u, \quad z = v,$$

as before. Here, therefore, the ratio is not completely determined, two of the quantities, say x and y, can be arbitrarily chosen; the chemical reaction is here a process depending upon *two* parameters.

Of course the choice is limited in that all the quantities must be positive. If we choose $x = 1$, then for y and z (and also for u and v) the condition must be fulfilled that $y + 2z = 1$ for positive y and z. If we assume y and z as coördinates (Fig. 15), then the condition $y + 2z = 1$ is fulfilled by all points on a straight line, and the further condition of positive value, by the points of this line which are in the first quadrant between the points AB of the line. We can, after choosing $x = 1$, choose y only smaller than 1 and z smaller than $1/2$.

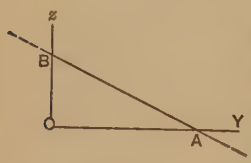


FIG. 15.

According to this it is apparent that the reacting amounts of substance in each chemical reaction is stoichiometrically given by equations of the form (4), of which there are as many as of chemical elements in

the reaction. If this number is n we have a simple chemical reaction, when $n - 1$ substances enter into the reaction equation (3). If s substances enter, then the equation depends upon $s - n$ parameters, for the n equations of each kind contain $s - 1$ proportions, and allow n of them to be made dependent upon the other $s - 1 - n$ proportions; hence upon $s - n$ arbitrary constants.

In the same way (as above example) that all possibilities of a reaction, depending upon two parameters, can be shown by the points of a line in the first quadrant, so can the points of a plane lying in the first octant show the possibilities of reactions depending upon three parameters.

From the reaction

$$x\mathrm{H} + y\mathrm{Cl} + z\mathrm{O} + t\mathrm{N} = u\mathrm{HCl} + v\mathrm{H_2O} + w\mathrm{NH_3}$$

follows the condition

$$x = u + 2v + 3w, \quad y = u, \quad t = w, \quad z = v,$$

that is, four conditions for seven unknown quantities.

If we choose $x = 1$ and u and v arbitrarily, then since

$$u + 2v + 3w = 1$$

w must be a positive number. If we imagine the w axis perpendicular to the plane of the paper (u, v), then only those values of u and v are available which give a positive value for w, that is, give a point in the surface lying in the positive octant; these points are those in the shaded triangle oAB (Fig. 16).

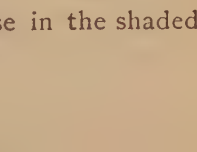


FIG. 16.

We see from this that for three independent variables we must give up these considerations.

It is enough to observe that

$$u + 2v - 1 = -3w$$

must be a negative quantity, and that is the case for all points u, v, of the triangle oAB, while for the points in the line AB the trinomial $u + 2v - 1 = 0$, is positive.

For four variables it is in this way possible to obtain help. It will be best illustrated by the example to which this method was first applied. Debus* (1882–91) treated the reaction of gunpowder as a chemical reaction which depends upon several variables, and Nickel† treated other chemical technical processes from the same standpoint.

Potassium nitrate, carbon (charcoal), and sulphur form by explosion potassium carbonate, sulphate, persulphid, carbonic acid gas, carbon monoxide and nitrogen, according to the reaction

$$x\mathrm{KNO_3} + y\mathrm{C} + z\mathrm{S} = t\mathrm{K_2CO_3} + u\mathrm{K_2SO_4} + v\mathrm{K_2S_2} + w\mathrm{CO_2} + a\mathrm{CO} + \tfrac{1}{2}x\mathrm{N_2}.$$

The equation is so written that one element, N, and one of the unknown quantities, viz., the number of mols of N, drop out of the equation; so that for the eight unknowns and the four elements we have the four conditions

$$\begin{aligned} x &= 2t + 2u + 2v, \\ y &= t + w + a, \\ z &= u + 2v, \\ 3x &= 3t + 4u + 2w + a; \end{aligned}$$

* Ann. d. chem. 212–265.

† Zeit. f. phys. chem, 1892 ff.

from which follows that

$$\begin{aligned} 7t &= \quad x + 2y - 4z - a, \\ 7u &= \quad 5x - 4y + \ z + 2a, \\ 14v &= -5x + 4y + 6z - 2a, \\ 7w &= -x + 5y + 4z - 6a. \end{aligned}$$

We choose, with Debus, $x = 16$, and ask how the other substances are to be chosen so that the reaction may be complete. We make use of the coördinate system (Fig. 17) y and z in the plane of the paper and a perpendicular to it. In this the planes

$$\begin{aligned} 0 &= 16 \quad + 2y - 4z - a, \\ 0 &= 80 \quad - 4y + \ z + 2a, \\ 0 &= -80 - 4y + 6z - 2a \end{aligned}$$

are to be marked, whose (Tafelspuren) intersection forms the triangle PQR. The planes themselves form a prism, whose edges project in the direction of y, and only those points lying *within* the prism have the coördinates y, z, a, which make the right sides of the above equations positive, and therefore t, u and v. In order that w may also be positive, the points must be chosen below the surface

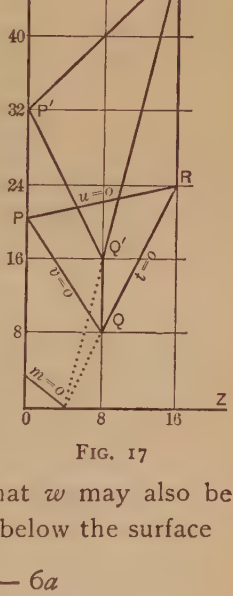


FIG. 17

$$0 = -16 + 5y + 4z - 6a$$

which belong to the points of the prism that are projected toward $P'Q'R'$ and which is formed by the

intersection of the line $w = 0$,—as is shown in the first principles of the solid analytical geometry.

We can now give by aid of the figure the amounts of substances necessary for a complete reaction. It is, for 16 mols saltpeter, as many mols of C and S as the coördinates of the points show which lie within the pentagon $P.QRR'P'$.

Debus limited himself to the amounts which were necessary for complete reaction without formation of carbon monoxide, by which $a = 0$. It is shown by the triangle PQR; and Debus has proved that all the new powders belong to this plane, while the older mixtures are represented by points outside of it.

The volume of gas developed (page 27) is

$$V = \left(w + a + \frac{x}{2}\right)22400 = \frac{22400}{28}(10x + 20y + 16z + 4a)\text{cc.}$$

for one of the composition

$$G = x\,.\,101 + y\,.\,12 + z\,.\,32 \text{ grams};$$

and the same quantity gave an amount of heat equal to

$$\begin{aligned} W &= t\,.\,279530 + u344640 + v108000 \\ &\quad + w97000 + a29000 - x119480 \\ &= 144196x - 16929y - 8783z - 11036a, \end{aligned}$$

where the heats of formation of the reacting substances occur as functions of the number of mols.

If we place again $x = 16$ and $a = 0$, it follows, as is not necessary to develop here, that the greatest

volume development takes place in point P, the greatest development of heat in point Q, as well when we use powders the same weights and also when they contain the same amounts of saltpeter. In the first case we find the greatest value for $\lambda = v:g$ and $\lambda' = w:g$; in the second the greatest value for V and W.

Here λ is proportional to the ratio in which the angle, formed by the lines $V = 0$ and $g = 0$, is divided by the line $V - \lambda g = 0$, and λ' has corresponding values.

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